

**DEVELOPMENT OF SYNTHETIC
METHODS OF ENVIRONMENTALLY
BENIGN HYPERVALENT IODINE
COMPOUNDS**

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**DEDICATED
TO
MY PARENTS**

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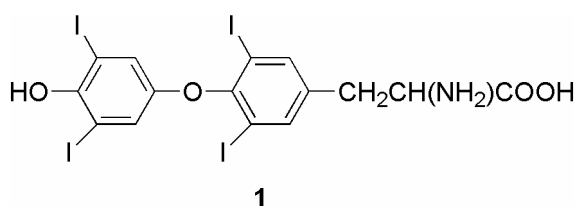
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Chapter I

a. Introduction

Iodine was discovered in 1811 by French chemist Bernard Courtois and it was named by J. L. Gay Lussac in 1813. Its name derives from the Greek word *iodes*, meaning "violet-colored," reflecting both the characteristic lustrous, deep purple color of resublimed crystalline iodine as well as the color of its vapor. Iodine is contained in seawater and soil as well as in the air in the form of iodide ion and other iodine derivatives. They are not suitable as raw materials for commercial iodine production, since their iodine concentration is very low. The iodine concentration in various types of seaweed is so high that they were used as the raw materials for iodine production in the early 1900's. The production is conducted only in areas where iodine concentration is high in brines from natural gas and oil fields, and in caliches from Niter at Chilean nitrate industry. Chile (59%) and Japan (32%) are the world's main producers of iodine. From the early beginning it found extremely useful applications in everyday life. It is known that potassium iodide was used as a remedy for goiter (Derbyshire neck), an enlargement of the thyroid gland, as early as 1819. The thyroid is responsible for the production of thyroxine **1**, a metabolism-regulating hormone.

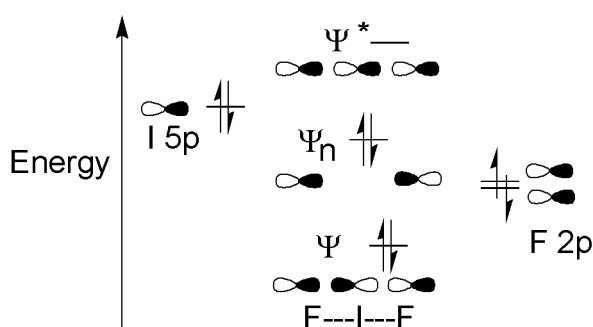


Iodine is an essential trace element for humans and plays an important role in many biological organisms. The most effective tincture of iodine is an alcohol solution of iodine and potassium iodide. Iodophores are iodine complexes with surfactants that act as iodine carriers. They are water soluble, less irritating to skin and other tissues than tincture. Iodine and

iodophores have a wide range of antimicrobial actions against gram positive and negative bacteria, tubercle bacilli, fungi, and viruses. The most popular iodophore for surgical scrub and gargle is povidone iodine, which contains about 10 percent iodine and release free iodine. It has virtually replaced tincture of iodine because they do not cause burning sensation when applied to raw tissue. Iodine uses commonly in halogen lamps, in ink pigments and as a topical antiseptic to kill bacteria. In addition, iodine is useful as an industrial catalyst and has many applications in the field of agriculture. Recently, demand for iodine has grown in high-tech fields such as LCD (liquid crystal display) polarizing film and etching agents for ITO (indium tin oxide).

Iodine is the largest, most polarizable, and least electronegative element of the common halogens, and also able to form stable polycordinate, multivalent compounds. Generally, compounds have the elements of 2, 8, or 18 electrons in valence shell by the Lewis-Langmuir's theory. However, hypervalent compounds are those which contain a main group element with more than an octet of electrons in its valence shell.¹ The first polyvalent organic iodine compound PhICl_2 was prepared by the German chemist Willgerodt² in 1886. These compounds were first described as hypervalent by Musher who laid out the foundations of their chemistry in a 1969 paper³ though their characteristic bonding had earlier been described by Pimentel in a 1951 report on bonding in trihalide anions⁴ and by Rundle in a report on the pentaiodide anion⁵ in the same year. The fundamental feature of these compounds is the highly polarized three-center-four-electron (3c-4e) bond, in which the central atom bears a positive charge and two monovalent ligands share the corresponding negative charge. This type of bonding serves to distinguish hypervalent compounds from transition metal complexes in which *d*-orbital hybridization is invoked to account for bonding beyond the stable octet.

The concept of hypervalent bonding was later supported by theoretical studies from Kutzelnigg⁶ in 1984 and Reed⁷ in 1990. These studies show that σ -bonding in higher main group elements (those beyond period 2) is significantly ionic and that d -orbitals are not directly involved in bonding. A simplified model of the hypervalent apical bond in IF_3 is shown in Figure 1.³ A $5p$ orbital of iodine overlaps with a $2p$ orbital of each fluorine to give a bonding orbital (ψ), a nonbonding orbital (ψ_n), and an antibonding orbital (ψ^*). The apical bond is longer and weaker than the equatorial bonds (1.983 \AA and 1.872 \AA , respectively),⁸ and in the HOMO, the electron density is localized on the fluorine atoms. Because of the polarized nature of the $3c-4e$ bond, ligands with higher electronegativity tend to occupy the apical positions in hypervalent compounds.



Hypervalent bond of IF_3

Figure 1

A broad variety of structural classes are known for iodine in oxidation states other than the common -1 . These polyvalent iodine species differ in the number of valence electrons (N) surrounding the central atom, the number of ligands (L) and their chemical nature. In terms of the Martin-Arduengo $N-X-L$ designation,⁹ four structural types of polyvalent iodine species, **2-5** (Figure 2) are the most important for organic chemistry. The first two species, **8-I-2** and **10-I-3** also called iodanes, are conventionally considered as derivatives of trivalent iodine,

and the last two, 10-I-4 and 12-I-5 periodanes, represent the most common structural types of pentavalent iodine. The most important classes and some of their parent members are shown in Table 1

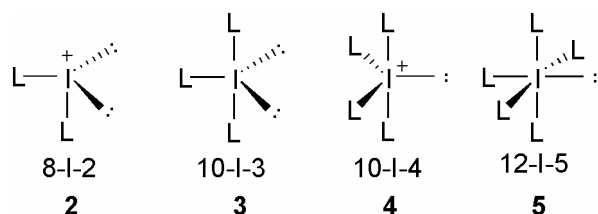


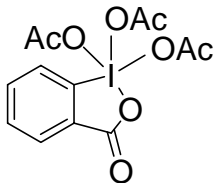
Figure 2 Structural types polyvalent iodine species

Table 1 Hypervalent Iodine Compounds

+3 Oxidation state

N-X-L Type	Example	Common Name
10-I-3	PhICl_2	(Dichloroiodo)benzene
10-I-3	$\text{PhI}(\text{OAc})_2$	(Diacetoxyiodo)benzene
8-I-2	Ph_2I^+	Diphenyliodonium
8-I-2	$\text{PhI}^+\text{CH}=\text{CH}_2$	Alkenyl(phenyl)iodonium
8-I-2	$\text{PhI}^+\text{C}\equiv\text{CH}$	Alkynyl(phenyl)iodonium
10-I-2	$\text{PhI}=\text{O}$	Iodosylbenzene
10-I-2	$\text{PhI}^+\text{HC}=\text{CXY}$	Phenyliodonium Methylides

+5 Oxidation state

N-X-L Type	Example	Common Name
12-I-3	PhIO ₂	Iodylbenzene
10-I-5		Des-Martin Reagent

The stability and reactivity of hypervalent iodine compounds exhibit a greater dependence on the character of hypervalent bonds in the apical position (Figure 3). The hypervalent bonds in the apical position are easily cleaved, and the cleavage causes trivalent iodine with 10 electrons to be reduced to monovalent iodine of a more stable octet structure. For this reason it exhibits good elimination and oxidation rates and finds application in organic synthesis.¹⁰

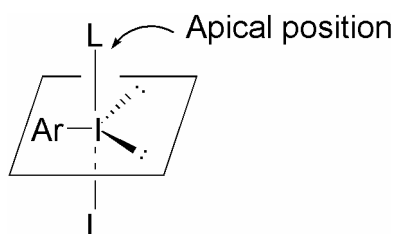


Figure 3

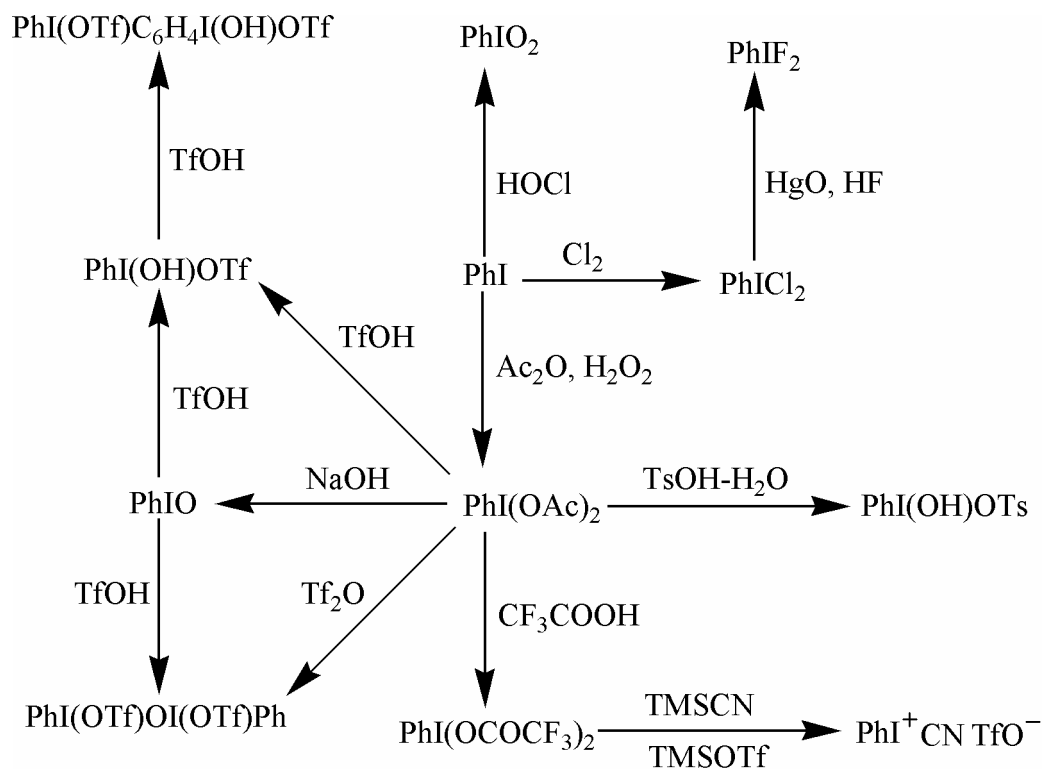
All hypervalent iodine reagents are solids-amorphous or crystalline-colorless and odorless. They are fairly stable at room temperature and insensitive to atmospheric oxygen and moisture. The usual precaution required upon storage is simply light-protection and sometimes refrigeration.

For several decades, iodanes were more chemical curiosities, devoid of any synthetic utility. However, the situation changed and presently many individual compounds as well as number

of classes are emerging as new valuable reagents in organic synthesis; among them are several heterocycles, the chemistry of which is often of exceptional interest. Because a lot of new reactions were developed, a somewhat enhanced degree of selectivity was inevitable. Several books¹¹ and review articles¹² are recently available for more detailed information. Another book by Varvoglis deals also specifically with synthetic applications.¹³

Preparative Methods for Hypervalent Iodine Reagents

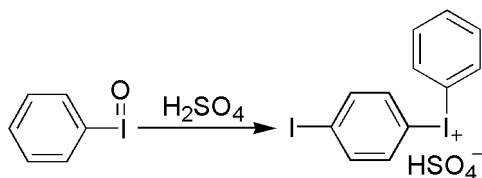
Most hypervalent iodine reagents are obtained from readily available starting materials, namely iodobenzene and ring substituted analogues; 2-iodobenzoic acid is the starting material for most heterocyclic iodanes. Several compounds are commercially available, but generally their preparation, with few exceptions, presents no special problems. Scheme 1 illustrates the main preparative approaches for iodobenzene derivatives. Some of them, such as PhICl_2 , PhIO , PhIO_2 , and $\text{PhI}(\text{OAc})_2$ appear in the Organic Syntheses. Interconversions among them occur readily and in several instances they offer improved procedures.



Ts = 4-MeC₆H₄SO₂, Tf = CF₃SO₂, TMS = Me₃Si

Scheme 1. Preparative Methods for Hypervalent Iodine Reagents Derived from Iodobenzene

Especially, new methods for preparation of various iodonium salts have been developed recently. In 1894, Hartmann and Meyer reported the generation of phenyl(*p*-iodophenyl)iodonium bisulfate (1.1) by the autocondensation of iodosobenzene in the presence of sulfuric acid, thus providing the first example of an organohalonium ion.¹⁴

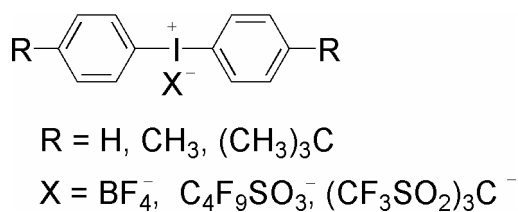


1.1

Most synthetic procedures for diaryliodonium salts involve the use of iodoxyarenes (ArIO₂)

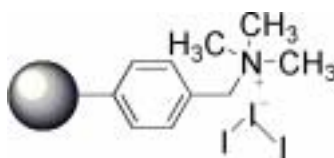
or members of the ‘iodoso’ family of compounds, i.e. the iodosoarenes (ArIO), (diacyloxyiodo)arenes [ArI(OCOR)₂], (dichloroiodo)arenes (ArICl₂) and related organoiodine(III) species.

Diaryliodonium salts are efficient photo-initiators for cationic polymerization. The hypervalent iodine compounds **6** are finding many applications, for example, photo-curable coating, printing ink and adhesives among many others. These compounds were modified to obtain appropriate physical properties such as melting points, solubilities, as well as UV absorption characteristics. They were also employed as photo-acid generators for use in the most sensitive photoresists used for integrated circuit fabrication.



6

Iodinated ion exchange resin (IER) **7** is the complex of I₃⁻ (hypervalent iodine) and anion exchange polymer. IER is a versatile solid antimicrobial agent with applications in drinking water disinfection, paints additives, air filtration products, and medical devices. IER interacts with microorganisms and immediately denature surface proteins of the microbe.

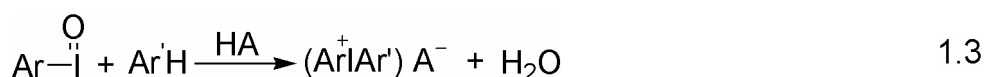
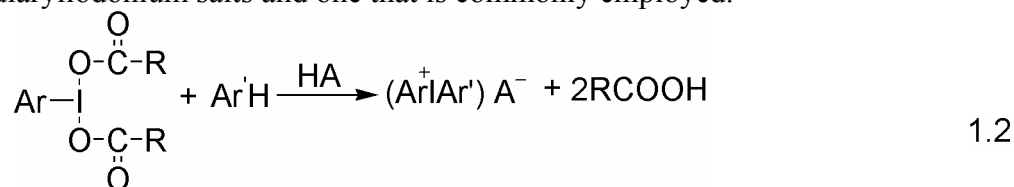


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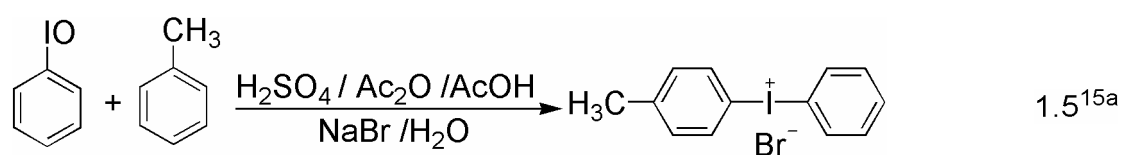
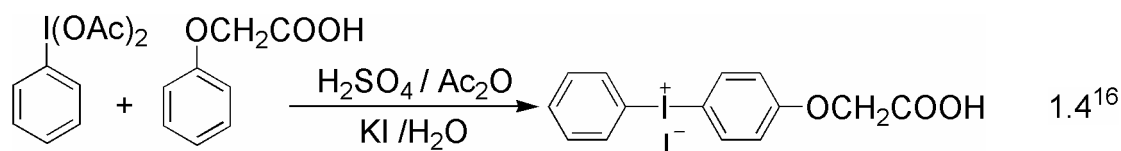
Diaryliodonium salts can be synthesized in a variety of ways. Several methods involve the

use of a strong acid medium while one classic procedure employs a basic medium, and still other methods require neutral organic solvents. Some procedures are specific for symmetrical iodonium salts while others provide access to unsymmetrical analogues. Some approaches permit the regiospecific placement of substituents in both rings of diaryliodonium salts; others do not. Some preparative methods of iodonium salts are described below:

The condensation of either iodosoarenes or (diacetoxyiodo)arenes, especially the diacetoxy analogues, with aromatic substrates in the presence of strong acid is a particularly versatile approach to diaryliodonium salts and one that is commonly employed.¹⁵

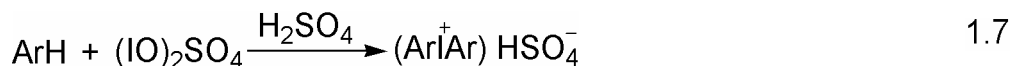


Example:

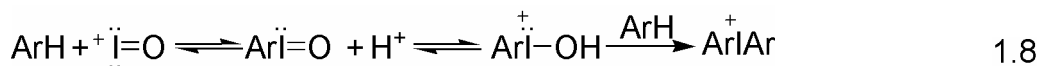


When molecular iodine and an alkali metal iodate are stirred in concentrated sulfuric acid, a yellow solid suspension of iodyl sulfate results.^{15a} The addition of aromatic substrates to such mixtures eventuates in the formation of symmetrical diaryliodonium bisulfates.^{15,17}

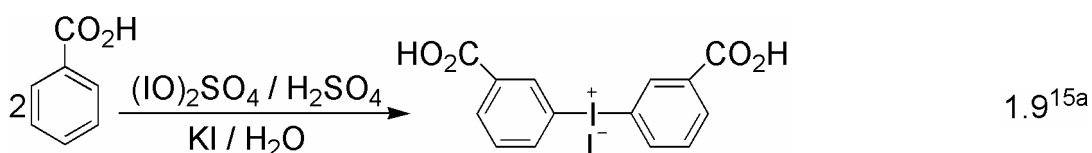




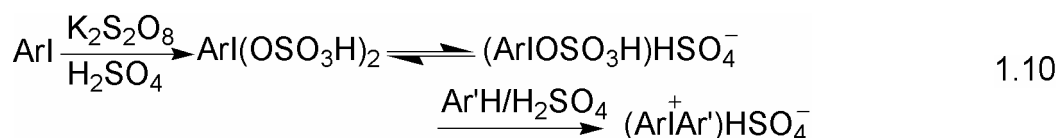
From a mechanistic standpoint, it seems likely that the iodyl cation first attacks an aromatic molecule to give an iodoso intermediate which then condenses with a second aromatic molecule in the manner already described.^{15b}



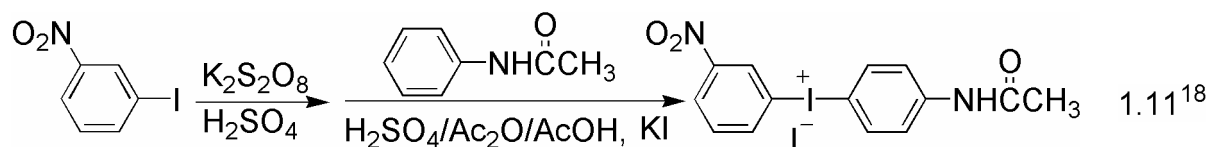
Example:



Treatment of iodoarenes first with potassium persulfate and then with aromatic substrates in sulfuric acid affords diaryliodonium salts. This method, which involves the in situ formation of 'iodoso' intermediates, is adaptable to the synthesis of symmetrical and unsymmetrical diaryliodonium compounds.^{15b}

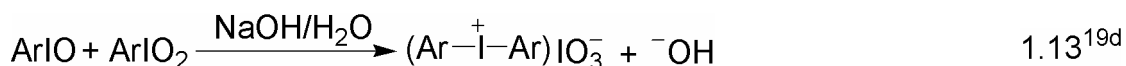
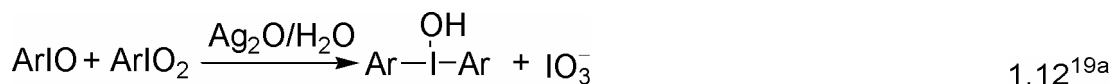


Example:

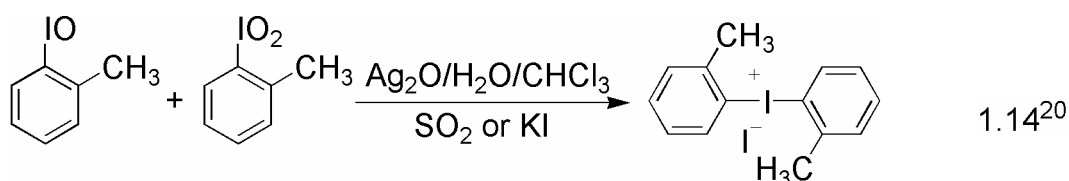


One classic approach to diaryliodonium salts, used extensively by early investigators, involves the condensation of an iodosoarene with an iodoxyarene in the presence of an

appropriate base.¹⁹ Such reactions are typically conducted in one of two ways: (a) a mixture of the iodoso- and iodoxyarenes in water is stirred with freshly prepared silver(I) oxide and (b) the iodoso- and iodoxyarenes are condensed in aqueous sodium hydroxide.



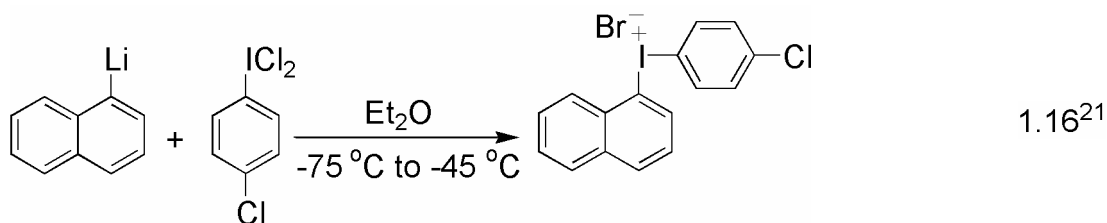
Example:



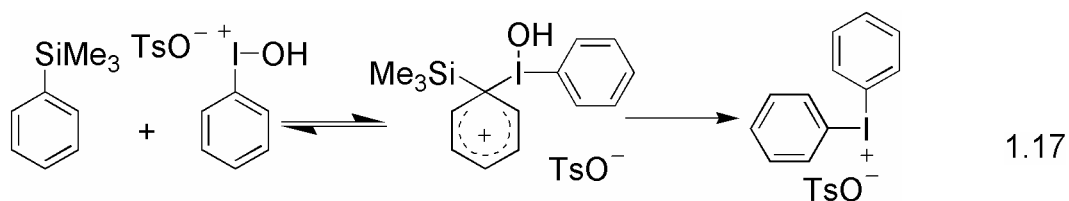
When (dichloroiodo)arenes are subjected to the action of aryllithium reagents in solvents such as ether or tetrahydrofuran (THF), diaryliodonium salts are obtained in moderate yields.²¹



Example:



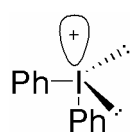
When [hydroxyl(tosyloxy)iodo]benzene and (trimethylsilyl)benzene are heated in acetonitrile, diphenyliodonium tosylate is obtained in 46% yield after workup.²²



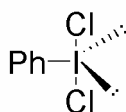
Structure and Bonding of Hypervalent Iodine Compounds

Generally, the structure of hypervalent iodine compounds is a trigonal bipyramid in the case of iodine (III) compounds and square bipyramid in the case of iodine (V) compounds.

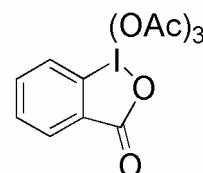
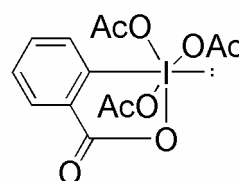
Structures of each type in hypervalent iodine compounds are shown below:



8-I-2

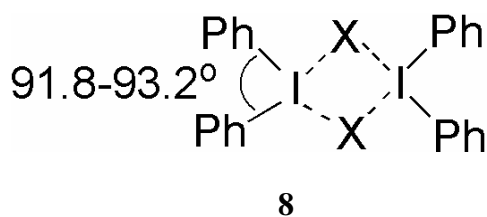


10-I-3



12-I-5

Diaryliodonium salts are not entirely ionic. This is true notably for the halides, which possess considerable covalent character in the crystalline state, while in aqueous solution they are not fully dissociated. Many crystal structure determinations have been carried out for several types of iodonium salts. With few exceptions, iodonium salts form dimers in which secondary bonds are developed. When the anion is highly electronegative (e.g., BF_4^-), it is far enough from iodine, so that there is a pronounced ionic character for such salts. The structures of diphenyliodonium salts containing chloride, bromide, and iodide as counteranion have been studied. All three are isomorphous centrosymmetric planar dimers **8** held together by halogen bridges. The C-I-X angles are close to 180° and the mean I-X bond distances are indicated below in comparison with normal “single” I-X bonds (in parentheses) and the sum of van der Waals radii (after the semicolon).

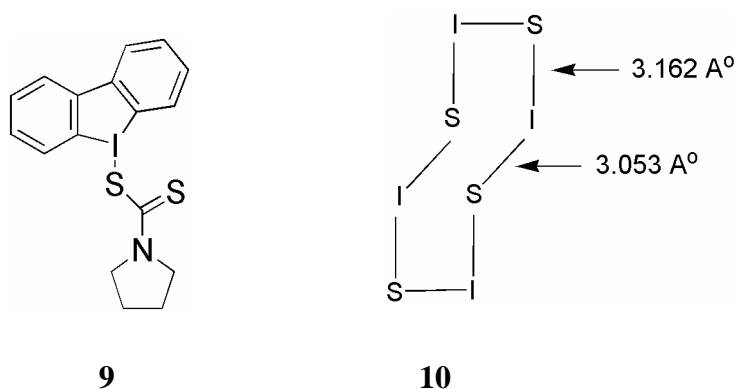


I-X bond distances (Å°)
 I-Cl 3.085, (2.321); 3.95
 I-Br 3.250, (2.185); 4.10
 I-I 3.437, (2.667); 4.30

Four I-X bond lengths in **8** are almost same and a common bond order of 0.35 has estimated for all three halides. Secondary hypervalent bonding appears to be equally effective in describing bonding qualitatively. The I-C bond distance in **8** is not affected significantly by the nature of the counteranion, ranging from 2.083 Å° for the bromide to 2.099 Å° for the iodide.²³ Two ionic diphenyliodonium salts have also been studied: in Ph₂IBF₄ the diphenyliodonium and tetrafluoroborate unites are not associated in pairs,²⁴ while in Ph₂INO₃ there are infinite *zig-zag* chains, -I-O...I'-O'-, extending through the structure.²⁵ The shortest secondary bonds in these salts are 2.94 Å° for I...F and 2.768 Å° for I...O. The I-C bond distances are 2.025 Å° for the tetrafluoroborate and 2.114 Å° for the nitrate.

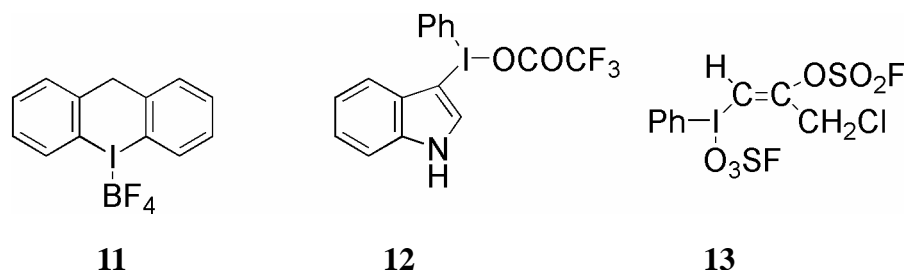
The unit cell of di(4-tolyl)iodonium bromide is unusual because it contains one dimer and one tetramer; in the latter an eight-membered pseudoring is formed made up of short (3.163 Å°) and long (3.513 Å°) I-Br bonds. The tetramer retains the dimer's planar geometry at I atom but the molecule is twisted at each Br atom, so that the next (4-tolyl)₂I unite is perpendicular to the previous one.²⁶

A dimeric structure with an eight-membered pseudoring of a chair conformation **10**, is observed²⁷ in dibenziiodonium dithiocarbamate **9**. The coordination around each I atom is planar-tetragonal comprising two normal I-C bonds (2.115 Å°) and two secondary I...S bonds, one short intermolecular (3.053 Å°), and one long (3.162 Å°) intramolecular, both significantly shorter than the sum of the van der Waals radii (3.78 Å°).



The presence of the iodonium ring caused a significant deviation in the linearity of the C-I-S angles from 180° (172.5 and 169.8°). A related compound $(4\text{-MeOC}_6\text{H}_4)_2\text{I}\cdots\text{SCSNEt}_2$, is monomeric,²⁸ forming a pseudo-four-membered ring with C-I-S angles of 176.0 and 125.8° . There are again two I...S secondary bonds, both intramolecular: one very short (2.927 Å) and one very long (3.285 Å). The properties of these compounds generally suggest that they may be described as covalent rather than ionic. Compound **9** and some related iodonium salts²⁹ have a C-I-C angle of 82° and their I-C bond distances are normal (2.120 Å in **9**, 2.08 Å in the tetrafluoroborate analogue). Six-membered dibenzoiodonium salts (e.g. **11**) have their heterocyclic ring in the boat conformation.³⁰

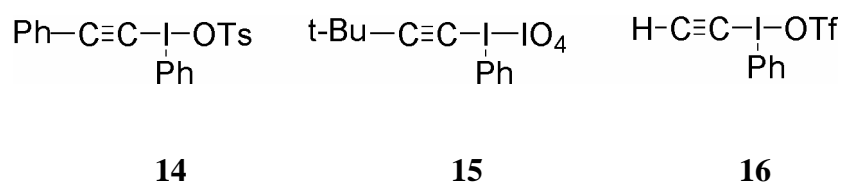
(3-Indolyl)(phenyl)iodonium trifluoroacetate **12** is monomeric,³¹ with a very short secondary I-O bond (2.735 Å); the sum of the van der Waals radii is 3.50 Å , while the covalent I-O bond length is 1.99 Å . Rather short is also the I-C indolyl bond (2.047 Å).



Some alkenyl(phenyl)iodonium salts were shown to be dimeric in the crystalline state,

forming eight membered pseudorings with the participation of both B and F atoms from the tetrafluoroborate anion³² or S and O atoms from the fluorosulfonate anion.³³ The latter salt **13** has a very short C=C bond (1.28 Å).

The alkynyl(phenyl)iodonium salt **14** has an I-O bond length of 2.56 Å (i.e. short for an ionic and long for a covalent bond). The I-C_{sp} bond is quite short (1.969 Å), while the I-C_{sp}² bond is longer than usual (2.120 Å), and the triple bond (1.181 Å) is within normal values.³⁴ The salt,³⁵ **15**, has similar features,³⁵ while in compound **16** the triple bond is very short³⁶ (1.141 Å).



Reaction of Hypervalent Iodine (III) Reagents

Many types of hypervalent iodine reagents have been used to organic synthesis. Among those hypervalent iodine reagents, the type of ArIX₂ have been available for synthetic purpose. The representative examples are given in Tables 2-6.

Table 2 Reactions with (Diacetoxyiodo)arenes

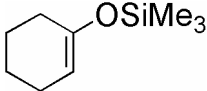
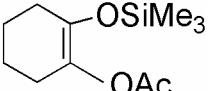
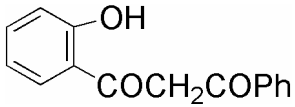
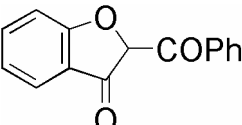
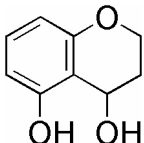
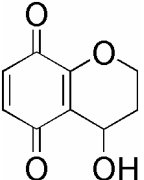
Entry	Substrate	Product	Reference
1			37
2			38
3			39
4	ArCOCH ₂ Me	ArCH(Me)CO ₂ Me	40
5	RCONH ₂	RNHCOOMe	41
6	R ₂ C=NOH	R ₂ CO	42
7	R ₂ C=NNH ₂	R ₂ CN ₂	43
8	ArCH=CH ₂	ArCOCH ₂ N ₃	44

Table 3 Reactions with [Bis(trifluoroacetoxy)iodo]arenes

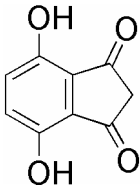
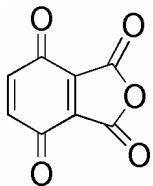
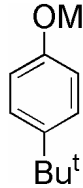
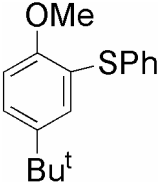
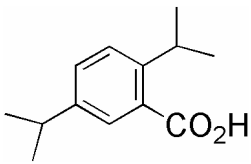
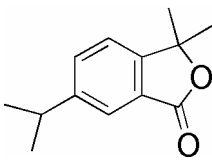
Entry	Substrate	Product	Reference
1			45
2			46
3			47
4	$\text{RC}\equiv\text{CH}$	RCOCH_2OH	48
5	RCOCH_3	RCOCH_2OH	49
6	RCONH_2	$\text{RNH}_3^+ \text{Cl}^-$	50
7	$\text{C}_8\text{H}_{17}\text{OCH}_2\text{Ph}$	$\text{C}_8\text{H}_{17}\text{O}_2\text{CCF}_3$	51

Table 4 Reactions with Iodosylarenes


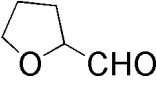
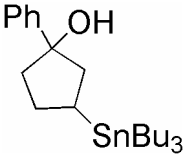
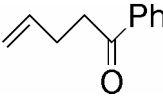
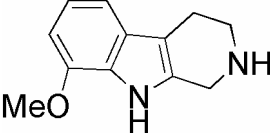
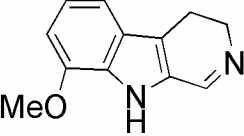
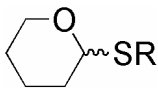
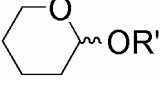
Entry	Substrate	Product	Reference
1			52
2			53
3			54
4			55
5	$\text{MeCOCH}_2\text{COMe}$	MeCOCH(OMe)COMe	56
6	$\text{RC}\equiv\text{CNMe}_2$	RCOCONMe_2	57
7	$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	$\text{ArCH}_2\text{CH}=\text{CH}_2$	58

Table 5 Reactions with (Dichloroiodo)arenes

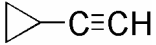
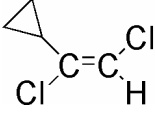
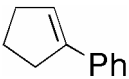
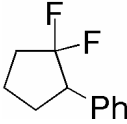
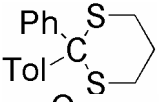
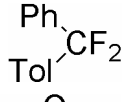
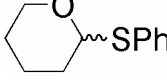
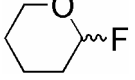
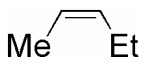
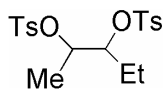
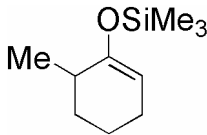
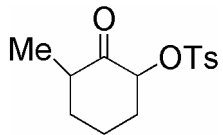
Entry	Substrate	Product	Reference
1	$\text{Me}_2\text{CHCHMe}_2$	$\text{Me}_2\underset{\text{Cl}}{\text{C}}\text{CHMe}_2$	59
2	$\text{MeCH}=\text{CHEt}$	$\text{Me}\underset{\text{Cl}}{\text{CH}}\underset{\text{Cl}}{\text{CH}}\text{Et}$	60
3			61
4	RSR	RSR	62
5	$\text{Ph}_3\text{P}=\underset{\text{COR}'}{\overset{\text{R}}{\text{C}}}$	$\text{Ph}_3\text{P}^+-\underset{\text{Cl}}{\overset{\text{R}}{\text{C}}}-\text{COR}' \text{Cl}^-$	63

Table 6 Reactions with (Difluoriodo)arenes

Entry	Substrate	Product	Reference
1	MeCH=CHCH=CH_2	$\text{MeCH=CHCH}_2\text{CHF}_2$	64
2			65
3			66
4			67

[Hydroxy(tosyloxy)iodo]benzene, $\text{PhI}(\text{OH})\text{OTs}$ (HTI), is often called Koser's reagent. It is a readily available stable compound gaining popularity in diverse fields. Its uses refer mostly to oxidations of various types and tosyloxyations (or oxysulfonylations with analogues bearing various RSO_3 groups), as shown in Table 7.

Table 7 Reactions with [Hydroxy(tosyloxy)iodo]benzene and its Analogues

Entry	Substrate	Product	Reference
1			68
2	$\text{PhC}\equiv\text{C}-\text{CH}_3$	$\text{PhCH}(\text{CH}_3)\text{CO}_2\text{H}$	69
3	$\text{RCOCH}_2\text{R}'$	$\text{RCOCH}(\text{OTs})\text{R}'$	70
4	RCONH_2	$\text{RNH}_3^+ \text{TsO}^-$	71
5			72

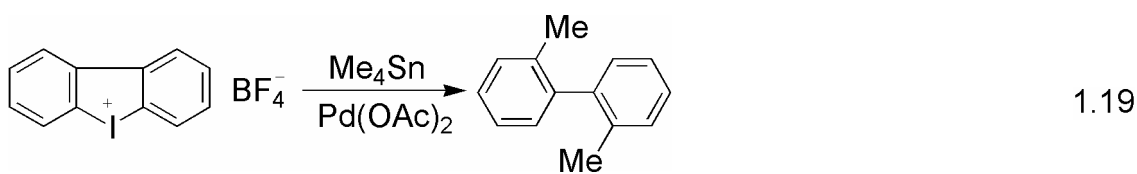
Reactions with Iodonium Salts and Its Analogues

Most iodonium salts are exceptionally stable and unreactive towards electrophiles and weak nucleophiles. These properties permit their transformation to other iodonium salts, by nitration, oxidation, etc. Exchange reactions between iodonium salts and lithiated arenes proceed through tris- and tetrakis-coordinated iodine (III) species and can lead to the formation of either symmetrical or unsymmetrical new iodonium salts.

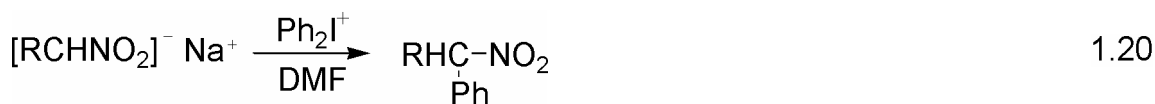
i) Arylation of Keto compounds⁷³



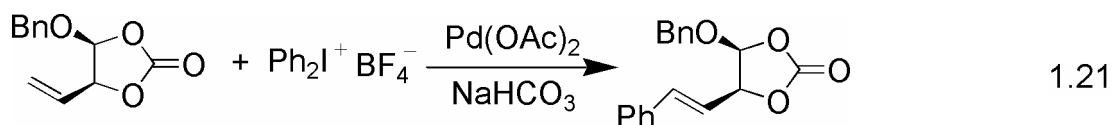
ii) Reactions with organometallics⁷⁴



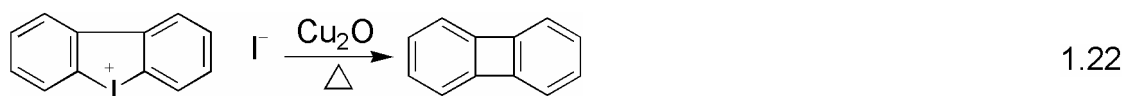
iii) Phenylation of nitro compounds⁷⁵



iv) Arylation of ethylenic compounds⁷⁶

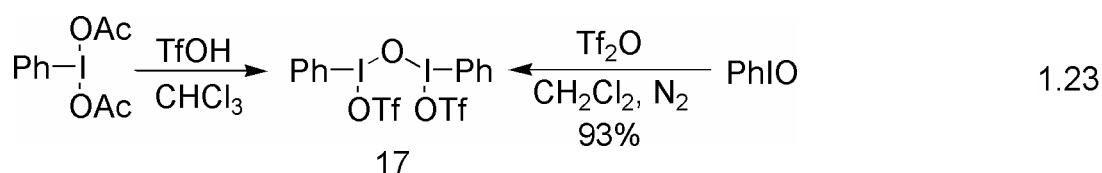


v) Synthesis of biphenylenes⁷⁷



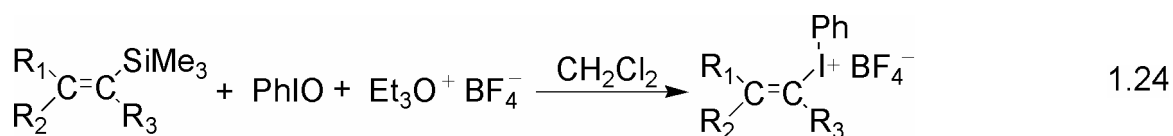
Preparation and Reaction of Zefirov's Reagent

The treatment of (diacetoxyiodo)benzene with trifluoromethanesulfonic acid does not give [hydroxy(trifluoromethylsulfonyloxy)iodo]benzene, $\text{PhI}(\text{OH})\text{OTf}$. When (diacetoxyiodo)benzene is mixed with trifluoromethanesulfonic acid in chloroform, the anhydride of $\text{PhI}(\text{OH})\text{OTf}$, μ -oxobis[(trifluoromethanesulfonyloxy)iodo]benzene **17** is obtained instead.⁷⁸ The treatment of iodosylbenzene with trifluoromethanesulfonic anhydride also affords **17**.⁷⁹ The oxygen bridged ditriflate **17** is a yellow solid, characteristic of some μ -oxoiodinanes,⁸⁰ and can be kept for months under nitrogen.⁷⁹



Preparation of Vinylodonium Salts

Petrakov and co-workers⁸¹ reported that vinylodonium salts were prepared from vinylmercury compounds or vinyltrichlorosilanes in low yields. Ochiai and co-workers reported that addition of the Meerwein reagent ($\text{Et}_3\text{O}^+ \text{BF}_4^-$) dropwise to the dichloromethane solution of vinylsilanes and iodosylbenzene gave vinylodonium salts in good yields.⁸²



b. Purpose and Objectives of This Work

The pollution of the environment is one of the global problems. The mass production of materials has contributed the improvement of living conditions to date, but such mass production caused high consumption and the global environmental problem. In order to

prevent the pollution and reduced the environment problems, chemists develop the safe and more environment-friendly chemical processes. The recent demand for highly efficient and environmentally-benign syntheses of fine chemicals and pharmaceuticals has encouraged the development of mild, safe, and highly chemoselective oxidizers.

Recently extensive studies on hypervalent iodine compounds such as (diacetoxyiodo)arenes, [bis(trifluoroacetoxy)iodo]arenes, [hydroxy(tosyloxy)iodo]arenes, polymer-supported hypervalent iodine compounds, Dess-Martin periodinane (DMP), diaryliodonium salts etc., are particularly suitable. The advantages of these reagents are high efficiency, easy availability, mild reaction conditions and (with the exception of DMP) stability against moisture and oxygen. The hypervalent iodine compounds are finding many applications, for example, photo-curable coating, printing ink and adhesives among many others. These compounds were modified to obtain appropriate physical properties such as melting points, solubilities, as well as UV absorption characteristics. They were also employed as photo-acid generators for use in the most sensitive photoresists used for integrated circuit fabrication.

In this thesis, the author carried out his research to develop novel synthetic methods of hypervalent iodine compounds and found three types novel procedures for (diacetoxyiodo)arenes, [bis(trifluoroacetoxy)iodo]arenes and diaryliodonium salts by using different conditions which is described in chapters II, III and IV.

Chapter II describes four preparative methods, A, B, C, and D, respectively. Method A presents the synthesis of (diacetoxyiodo)arenes, $\text{ArI}(\text{OAc})_2$, from iodoarenes with $\text{K}_2\text{S}_2\text{O}_8$ in acetic acid in the presence of concd H_2SO_4 or $\text{CF}_3\text{SO}_3\text{H}$ at room temperature (25°C). Method B generates (diacetoxyiodo)arenes from iodoarenes with sodium perborate in acetic acid in the presence of triflic acid at $40\text{--}45^\circ\text{C}$. In Method C, poly[4-(diacetoxyiodo)styrene] produces

from poly(4-iodostyrene) by using AcOH, 1,2-dichloroethane and CF₃SO₃H in the presence of NaBO₃ at 44-45 °C. Method D affords (diacetoxyiodo)arenes in the reaction of arenes with K₂S₂O₈, elemental iodine, 1,2-dichloroethane and acetic acid in the presence of concd H₂SO₄ at 40 °C.

Chapter III describes an effective method for preparing [bis(trifluoroacetoxy)iodo]arenes, ArI(OCOCF₃)₂, from some iodoarenes using K₂S₂O₈/CF₃COOH/ CH₂Cl₂ system at 36-38 °C.

Chapter IV represents three synthetic methods A, B, and C. In Method A, Diaryliodonium triflates directly prepare from some iodoarenes with aromatic substrates by using K₂S₂O₈/CF₃COOH/CH₂Cl₂ system at 36-38 °C, followed by treatment with NaOTf solution at r. t. In method B, diaryliodonium triflates generate directly by reaction of arenes with elemental iodine in good yields by using K₂S₂O₈/CF₃COOH/ClCH₂CH₂Cl system at 40 °C. In method C, diaryliodonium triflates form by reaction of arenes with elemental iodine by using K₂S₂O₈, AcOH and TfOH at 40 °C in one-pot procedure. Diaryliodonium tosylates also afford from arenes and elemental iodine by using K₂S₂O₈, AcOH, H₂SO₄ and TsOH at 40 °C in one-pot procedure.

c. References

1. Akiba, K. In Chemistry of Hypervalent Compounds; Akiba, K., Ed.; VCH Publishers: New York, **1999**, 1-8.
2. Willgerodt, C. *J. Prakt. Chem.* **1886**, 33, 154.

3. Musher, J. I. *Angew. Chem. Int. Ed.* **1969**, 8, 54.
4. Pimentel, G. C. *J. Chem. Phys.* **1951**, 19, 446.
5. Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, 73, 4321.
6. Kutzelnigg, W. *Angew. Chem. Int. Ed.* **1984**, 23, 272.
7. Reed, A. E.; von Rague Schleyer, P. J. *J. Am. Chem. Soc.* **1990**, 112, 1434.
8. Hoyer, S; Seppelt, K. *Angew. Chem. Int. Ed.* **2000**, 39, 1448.
9. Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Law, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, 102, 7753.
10. a) Varvoglis, A. *Synthesis* **1984**, 709. b) Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* 1996, 96, 1123. c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, 102, 2523.
11. a) Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: Weinheim, **1992**.
b) Zhdankin, V. V.; Stang, P. J. *Chemistry of Hypervalent Compounds* Akiba, K-y. Eds.; John Wiley & Sons, New York, **1998**; Chapters 11 and 12.
12. a) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. b) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 274. c) Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221. d) Prakash, O.; Saini, N.; Sharma, P. K. *Heterocycles* **1994**, 221. e) Stang, P. J., In *The chemistry of Triple-bonded Functional Groups, Supplement C2*; Patai, S., Ed.; John Wiley and Sons, Ltd.: Chichester, **1994**; Vol. 2, Chapter 20, p. 1164. f) Stang, P. J., In *Modern Acetylene Chemistry*; Stang, P. J.; Diederich, F. Eds.; VCH Publishers: Weinheim, **1995**; Chapter 3, p. 67. g) Koser, G. F., Halonium Ions, in *The Chemistry of Functional Groups, Supplement D2*, Patai, S.; Rappoport, Z., Eds.; John Wiley and Sons, Ltd.: Chichester, **1983**, Chapter 25, p. 1265. h) Varvoglis, A. *Chimica Chronica* **1995**, 24, 3. i) Varvoglis, A. *Tetrahedron* **1997**, 53, 1179. j) Kitamura, T.; Fujiwara, Y. *Org. Prep. Proced. Int.* **1997**, 29, 409. k) Varvoglis, A.; Spyroudis,

S. Synlett **1998**, 221.

13. Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, **1996**.

14. Hartmann, C.; Meyer, V. *Chem. Ber.* **1894**, 27, 426.

15. a) Beringer, F. M.; Drexler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* **1953**, 75, 2705. b) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, 81, 3819.

16. Beringer, F. M.; Falk, R. A. *J. Am. Chem. Soc.* **1959**, 81, 2997.

17. a) Masson, I.; Hanby, W. E. *J. Chem. Soc.* **1938**, 1699. b) Masson, I.; Race, E. *J. Chem. Soc.* **1937**, 1718. c) Masson, I.; Argument, C. *J. Chem. Soc.* **1938**, 1702.

18. Beringer, F. M.; Lillien, I. *J. Am. Chem. Soc.* **1960**, 82, 725.

19. a) Willgerodt, C. *Die organischen Verbindungen mit mehrwertigem Jod*, F. Enke, Stuttgart, **1914**. b) Sandin, R. B. *Chem. Rev.* **1943**, 32, 249. c) Banks, D. F. *Chem. Rev.* **1966**, 66, 243. d) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* **1955**, 3, 355.

20. Lucas, H. J.; Kennedy, E. R.; Wilmot, C. A. *J. Am. Chem. Soc.* **1936**, 58, 157.

21. Beringer, F. M.; Dehn, Jr, J. W.; Winicov, M. *J. Am. Chem. Soc.* **1960**, 82, 2948.

22. Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, 45, 1543.

23. Alclock, N. W.; Countrymann, R. M. *Dalton Trans.* **1997**, 217.

24. Struchkov, Y. T.; Khotsyanova, T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 821.

25. Wright, W. B.; Meyers, E. A. *Cryst. Struct. Commun.* **1972**, 1, 95.

26. Alclock, N. W.; Countrymann, R. M. *J. Chem. Soc. Dalton Trans.* **1987**, 193.

27. Bozopoulos, A. P.; Rentzeperis, P. J. *Acta Crystallogr.* **1986**, C42, 1014.

28. Bozopoulos, A. P.; Rentzeperis, P. J. *Acta Crystallogr.* **1987**, C43, 914.

29. Beringer, F. M.; Ganis, P.; Avitabile, G.; Jaffe, H. H. *J. Org. Chem.* **1972**, 37, 879.

30. Alliev, Z. G.; Atovmyan, L. O.; Egorova, L. D.; Lisichkina, I. N.; Tolstaya, T. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 1042.
31. Petrov, V. N.; Lindermann, S. V.; Struchkov, Y. T.; Chugtai, F. A.; Budylin, V. A.; Bundel, Y. G. *Dokl. Akad. Nauk SSSR* **1983**, 269, 614.
32. Ochiai, M.; Sumi, K.; Takaoka, Y.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, 44, 4095.
33. Chekhlov, A. N.; Gafurov, R.G.; Pomytkin, I. A.; Martynov, I. V.; Aleinikov, N. N.; Kashtanov, S. A.; Dubovitskii, F. I. *Dokl. Akad. Nauk SSSR* **1986**, 291, 414.
34. Stang, P. J.; Surber, B. W.; Chen, Z. -C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, 109, 228.
35. Ochiai, M.; Kunishima, M.; Fuji, K.; Nagao, Y.; Shiro, M. *Chem. Pharm. Bull.* **1989**, 37, 1948.
36. Stang, P. J.; Arif, A. M.; Crittall, C. M. *Angew. Chem. Int. Ed. Engl.* **1990**, 29, 287.
37. Brunolevskaya, I. I.; Kussainova, K. M.; Kashin, A. K. *Zh. Org. Khim.* **1988**, 24, 358.
38. Prakash, O.; Goyal, S.; Pahuja, S.; Singh, S. P. *Synth. Commun.* **1990**, 20, 1409.
39. Saitz, C. B.; Valderrama, J. A.; Tapia, R.; Farina, F.; Paredes, M. C. *Synth. Commun.* **1992**, 22, 955.
40. Tamura, Y.; Yakura, T.; Shirouchi, Y.; Haruta, J. *Chem. Pharm. Bull.* **1985**, 33, 1097.
41. Moriarty, R. M.; Chany, II, C. J.; Vaid, R. K.; Prakash, O.; Tuladhar, S. M. *J. Org. Chem.* **1993**, 58, 2478.
42. Moriarty, R. M.; Prakash, O.; Vavilikolanu, P. R. *Synth. Commun.* **1986**, 16, 1247.
43. Smith, P. A. S.; Bruckmann, E. M. *J. Org. Chem.* **1974**, 39, 1047.
44. Ehrenfreund, J.; Zbiral, E. *Tetrahedron* **1972**, 28, 1697.

45. Kanematsu, K.; Morita, S.; Fukushima, S.; Osawa, E. *J. Am. Chem. Soc.* **1981**, *103*, 5211.
46. Kita, Y.; Takada, T.; Mihara, S.; Tohma, H. *Synlett* **1995**, 211.
47. Togo, H.; Muraki, T.; Yokohama, M. *Tetrahedron Lett.* **1995**, *36*, 7089.
48. Kita, Y.; Yakura, T.; Terashi, H.; Haruta, J.; Tamura, Y. *Chem. Pharm. Bull.* **1989**, *37*, 891.
49. Moriarty, R. M.; Berglund, B. A.; Penmasta, R. *Tetrahedron Lett.* **1992**, *33*, 6065.
50. Loudon, G. M.; Radhakrishna, A. S.; Almond, M. R.; Blodgett, J. K.; Boutin, R. H. *J. Org. Chem.* **1984**, *49*, 4272.
51. Spyroudis, S.; Varvoglis, A. *J. Chem. Soc. Chem. Commun.* **1979**, 615.
52. Zefirov, N. S.; Caple, R.; Palyulin, V. A.; Berglund, B.; Tykwinski, R.; Zhdankin, V. V.; Kozmin, A. S. *Izv, Akad. Nauk SSSR* **1988**, 1452.
53. Ochiai, M.; Ukita, T.; Iwaki, S.; Nagao, Y.; Fujita, E. *J. Org. Chem.* **1989**, *54*, 4832.
54. Porta, F.; Crotti, C.; Cennini, S.; Palmisano, G. *J. Mol. Cat.* **1989**, *50*, 333.
55. Fukase, K.; Hasuoka, A.; Kinoshita, I.; Kusumoto, S. *Tetrahedron Lett.* **1992**, *33*, 7165.
56. Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Hopkins, T. E. *Tetrahedron* **1988**, *44*, 1603.
57. Muller, P.; Godoy, J. *Tetrahedron Lett.* **1982**, *23*, 3661.
58. Lee, K.; Kim, D. Y.; Oh, Y. *Tetrahedron Lett.* **1988**, *29*, 667.
59. Arase, A.; Hoshi, M.; Masuda, Y. *Chem. Lett.* **1979**, 961.
60. Devillier, M.; Bodot, H. *Bull. Soc. Chim. Fr.* **1972**, 227.
61. Shellhamer, D. F.; Oakes, M. L. *J. Org. Chem.* **1978**, *43*, 1316.
62. Barbieri, G.; Cinquini, M.; Colonna, S.; Montanari, F. *J. Chem. Soc. (C)* **1968**, 659.
63. Zbiral, E.; Raspberger, M. *Tetrahedron* **1969**, *25*, 1871.
64. Shellhamer, D. F.; Conner, R. J.; Richardson, R. E.; Heasley, V. L. *J. Org. Chem.* **1984**, *49*,

5015.

65. Gregorcic, A.; Zupan, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 517.
66. Motherwell, W. B.; Wilkinson, J. A. *Synlett* **1991**, 191.
67. Caddick, S.; Gazzard, L.; Motherwell, W. B.; Wilkinson, J. A. *Tetrahedron* **1996**, *52*, 149.
68. Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 2462.
69. Moriarty, R. M.; Vaid, R. K.; Duncan, M. P.; Vaid, B. K. *Tetrahedron Lett.* **1987**, *28*, 2845.
70. Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487.
71. Vasudevan, A.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 5158.
72. Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101.
73. Chen, K.; Koser, G. F. *J. Org. Chem.* **1991**, *55*, 5764.
74. Bumagin, N. A.; Sukhomlinova, L. I.; Igushkina, S. O.; Vanchikov, A. V.; Tolstaya, T. P.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR* **1992**, 2683.
75. Kornbloom, N.; Taylor, H. J. *J. Org. Chem.* **1963**, *28*, 1424.
76. Kang, S.-K.; Jung, K.-Y.; Park, C.-H.; Jang, S.-B. *Tetrahedron Lett.* **1995**, *36*, 8047.
77. Baker, W.; Boorland, M. P. V.; McOmie, J. F. W. *J. Chem. Soc.* **1954**, 1476.
78. Zefirov, N. S.; Zhdankin, V. V.; Dan'kov, Y. V.; Koz'min, A. S. *J. Org. Chem. USSR (Engl. Trans)* **1984**, *20*, 401.
79. Hembre, R. T.; Scott, C. P.; Norton, J. R. *J. Org. Chem.* **1987**, *52*, 3650.
80. Gallos, J.; Varvoglis, A.; Alcock, N. W. *J. Chem. Soc. Perkin Trans. I* **1985**, 757.
81. a) Nesmeyanov, A. N.; Tolstaya, T. P.; Sokolova, N. F.; Varfolomeeva, V. N.; Petrakov, A. V. *Dokl. Akad. Nauk SSSR* **1971**, *198*, 115. b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A.

V.; Goltsev, A. N. *Dokl. Akad. Nauk SSSR* **1977**, 235, 591. c) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, L. F. *Dokl. Akad. Nauk SSSR* **1978**, 238, 1109.

82. Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, 26, 2351.

Chapter II

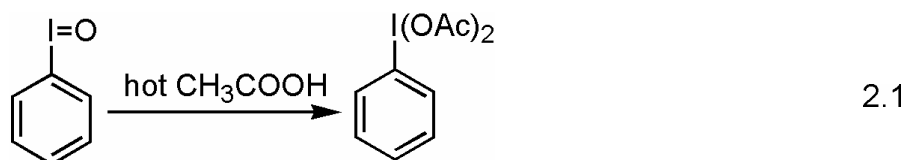
Preparation of (Diacetoxyiodo)arenes

A. Easy Preparation of (Diacetoxyiodo)arenes from Iodoarenes

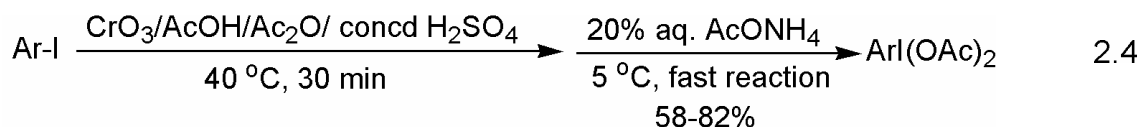
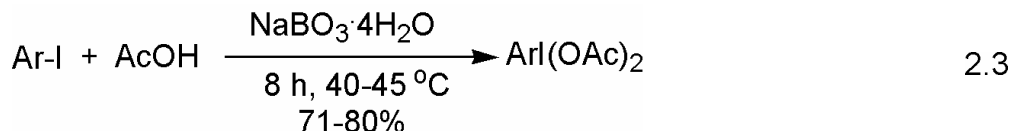
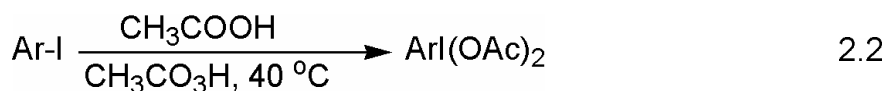
Using Potassium Peroxodisulfate as the Oxidant

a. Introduction

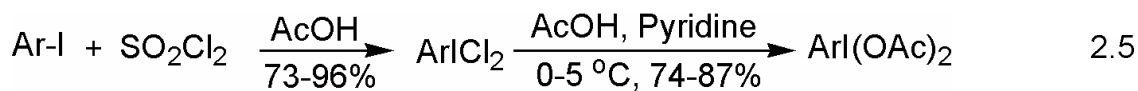
Over the last past decade, the use of hypervalent iodine reagents has gained importance as mild oxidants for performing a variety of organic transformations. (Diacetoxyiodo)arenes, $\text{ArI}(\text{OAc})_2$, and particularly the parent compound, (diacetoxyiodo)benzene, $\text{PhI}(\text{OAc})_2$, have been known for a long time.¹⁻⁵ They are received a great deal of attention due to low toxicity, ready availability, easy handling and reactivity similar to that of heavy metal reagents and anodic oxidation. They are potent, often chemoselective oxidants, widely used in modern organic synthesis. They are also used for the facile synthesis of, for example, iodosylarenes, [bis(trifluoroacetoxy)iodo]arenes, [hydroxyl(tosyloxy)iodo]]arenes (selective oxidants) and aromatic iodonium salts (arylation reagents), etc.²⁻⁶ Historically, the first member, (diacetoxyiodo)benzene was synthesized by Willgerodt in 1892, by dissolving iodosylbenzene in hot acetic acid (2.1).⁷



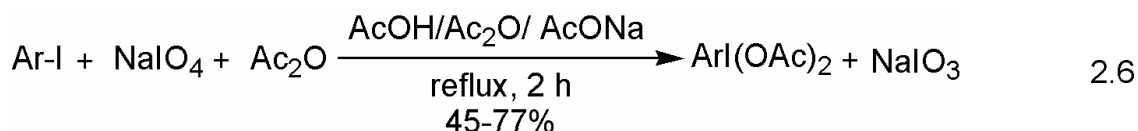
Iodoarenes are oxidized in warm glacial acetic acid by either peracetic acid (2.2),⁵ sodium perborate tetrahydrate (2.3),⁸ chromium(VI)oxide (2.4).⁹ or electrolytically.^{3,4}



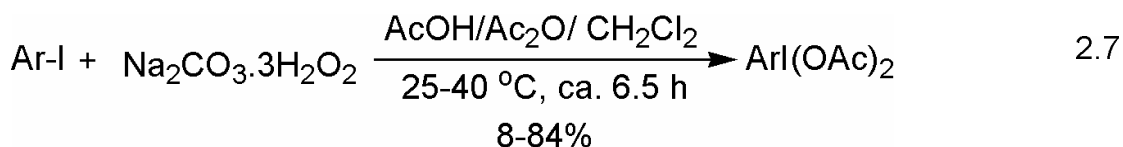
Iodoarenes are converted to (diacetoxyiodo)arenes by two-step reaction: reaction with sulfonyl chloride to yield dichloroiodoarenes followed by treatment with aqueous acetic acid in pyridine (2.5).¹⁰



Iodoarenes are refluxed for 2 h in NaIO₄/AcOH/Ac₂O/AcONa solutions to give finally the purified ArI(OAc)₂ (2.6).¹¹

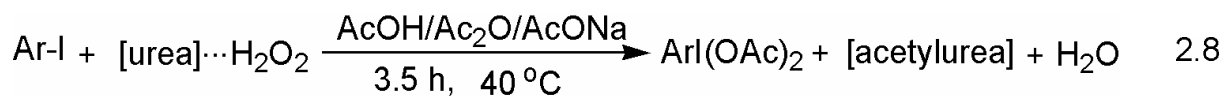


Iodoarenes are oxidized by using sodium percarbonate in an anhydrous ternary solvent system: Ac₂O/AcOH/CH₂Cl₂ (2.7).¹²



The reactions underwent in anhydrous mixtures, AcOH/Ac₂O/AcONa (a catalyst) in the presence of commercially available and easily handled urea-hydrogen peroxide adduct as the

oxidant at 40 °C for 3.5 h to afford the purified ArI(OAc)₂ in 37-78% yields (2.8).¹³



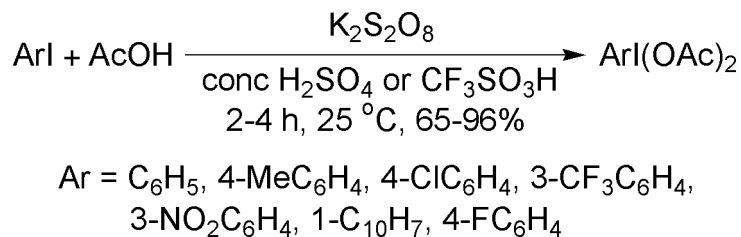
The standard, and most general, method for the synthesis of ArI(OAc)₂ (oxidative diacetoxylation of ArI by warm peracetic acid solution) is, in fact, a very prolonged reaction (12-16 h), and the utmost care should be taken to maintain the exact temperature, 40 °C. Two-step conversion of various ArI to ArI(OAc)₂ in the anhydrous CrO₃/AcOH/Ac₂O/concd H₂SO₄ liquid system, followed by mixing with excess 20% aqueous ammonium acetate solution. This procedure is 8-16 times faster and ca. 5 times less expensive than the method of McKillop and Kemp.⁸ However, this method is hardly applicable for iodotoluenes [4-MeC₆H₄I(OAc)₂ was obtained from 4-MeC₆H₄I in only 20% yield]. For ArI substituted with strong electron withdrawing groups, the sodium periodate system is not applicable.¹¹ In sodium percarbonate method,¹² 4-iodotoluene and 4-chloriodobenzene were unexpectedly oxidized to the corresponding iodylarenes. Here, an alternative, easy method for preparation of (diacetoxyiodo)arenes from iodoarenes were reported.

b. Results and Discussion

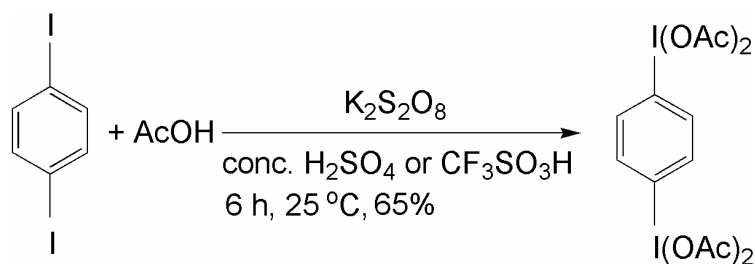
A quick and efficient method for preparing ArI(OAc)₂ were presented in high yields within short time from the corresponding iodoarenes in AcOH, using commercial potassium peroxodisulfate, K₂S₂O₈, as the oxidant. The results are given in Table 2.1. Addition of concd H₂SO₄ or CF₃SO₃H is essential to generate (diacetoxyiodo)arenes. K₂S₂O₈ is used as a strong oxidizing agent in many applications. It has the particular advantages of being almost non-hygroscopic, a particular good storage stability, and ease and safe of handle. The oxidation of iodoarenes to (diacetoxyiodo)arenes can be easily scaled up, and given the advantages of

$K_2S_2O_8$ outlined above, together with the complete absence of effluent or byproduct problems.

The novel method is described in Scheme 2.1



Scheme 2.1



Scheme 2.2

Table 2.1 Preparation of (Diacetoxyiodo)arenes from Iodoarenes^a

Entry	Iodoarenes	Additives (mmol)	Time (h)	Yield(%)
1	C_6H_5I	H_2SO_4 (4)	2	95.7
2 ^b	C_6H_5I	H_2SO_4 (100)	4	88.7
3	4-Me C_6H_4 -I	H_2SO_4 (4)	2	75.2
4	4-Cl C_6H_4 -I	H_2SO_4 (4)	2	74.4
5	3-CF $_3C_6H_4$ -I	CF $_3SO_3H$ (6)	4	77.9
6	3-NO $_2C_6H_4$ -I	CF $_3SO_3H$ (6)	4	72.9
7	1-IC $_{10}H_7$	H_2SO_4 (4)	4	85.4
8	1,4-I $_2C_6H_4$	CF $_3SO_3H$ (6) ^c	6	65.3
9	4-FC $_6H_4$ -I	H_2SO_4 (4)	4	70.7

^aThe reaction of an iodoarene (1 mmol) was carried out in AcOH (5 mL) in the presence of K₂S₂O₈ (4 mmol) at 25 °C.

^bIodoarene (5.1 g, 25 mmol), K₂S₂O₈ (100 mmol), and AcOH (125 mL).

^cCH₂Cl₂ (3 mL) was added.

The oxidative reactions shown in Schemes 2.1 and 2.2 were carried out at room temperature (25 °C), in a mixture of AcOH and concd H₂SO₄ or CF₃SO₃H. The presence of K₂S₂O₈ (in stoichiometric quantities) in the reaction mixture was indispensable because without its addition the oxidation reactions did not proceed. When K₂S₂O₈ was replaced for sodium peroxodisulfate, Na₂S₂O₈, the final yields of ArI(OAc)₂ were lowered by ca. 11-16%. Iodoarenes bearing strong electron-withdrawing groups such as trifluoromethyl and nitro at the *meta* position also gave (diacetoxyiodo)arenes in good yields, but the reaction of 1-iodo-4-nitrobenzene and 1-iodo-3,5-bis(trifluoromethyl)benzene resulted in low yields (18-20%) of (diacetoxyiodo)arenes due to their decreased reactivity. This method was not applicable for iodoarenes with strong electron-donating groups. For example, iodoanisoles were quickly oxidized in the reaction mixtures, but the reaction resulted in the decomposition and the formation of tarry products. This method was also unaffected for trisubstituted iodoarenes due to the steric effect of the multiple substituents.

c. Experimental Section

General

Melting points were determined with a Yanaco micro-melting point apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-AL300

spectrometer and the chemical shifts were expressed in parts per million downfield from tetramethylsilane.

Optimized Procedure for Preparing (Diacetoxyiodo)arenes from Iodoarenes

$K_2S_2O_8$ (4 mmol) was slowly added portionwise during 10 min to a stirred solution of an iodoarene (1 mmol) in AcOH (5 mL) with concd H_2SO_4 (4 mmol) or CF_3SO_3H (6 mmol) at room temperature (25 °C), and the mixture was stirred at room temperature until TLC analysis indicated completion of reaction. In the case of 1,4-diiodobenzene, CH_2Cl_2 (3 mL) was added for dissolving 1,4-diiodobenzene completely. Reaction times varied from 2 h for iodobenzene to maximum 6 h for other iodoarenes. The solution was then concentrated to half its volume by evaporation of AcOH under reduced pressure, and H_2O (10 mL) was added. The resulting precipitate was collected by filtration, washed with H_2O (10 mL), and dried in air. A second crop of product was obtained by extraction of the filtrate with CH_2Cl_2 (3×10 mL) and the combined extracts were dried over anhyd Na_2SO_4 ; after filtration the solution was concentrated under reduced pressure. The combined crude products were purified by recrystallization from AcOH/hexane.

Preparation of (Diacetoxyiodo)benzene; Large Scale

$K_2S_2O_8$ (100 mmol) was slowly added portionwise over 20 min to a stirred solution of an iodobenzene (5.1 g, 25 mmol) in AcOH (125 mL) with concd H_2SO_4 (100 mmol) at r. t. (25 °C), and the mixture was stirred at r. t. for 4 h. The solution was then concentrated to half its volume by evaporation of AcOH under reduced pressure, and water (100 mL) was added. The precipitate formed was collected by filtration, washed with H_2O (200 mL), and dried in air. A second crop of product was obtained by extraction of the filtrate with CH_2Cl_2 (3×25 mL); the combined extracts were dried over anhyd Na_2SO_4 , filtered, and concentrated under reduced

pressure. The combined crude products were purified by recrystallization from AcOH/hexane; yield: 7.15 g (88.7%).

(Diacetoxyiodo)benzene

Yield: 0.304 g (95.7%); mp 162-163 °C (lit.¹⁴ mp 161.1-162.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.47-7.53 (m, 2 H, ArH), 7.58-7.64 (m, 1 H, ArH), 8.07-8.12 (m, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.19, 134.77, 131.58, 130.79, 121.36, 20.18.

1-(Diacetoxyiodo)-4-methylbenzene

Yield: 0.250 g (75.2%); mp 106-108 °C (lit.¹⁴ mp 106-110 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.00 (s, 6 H, MeCO₂), 2.44 (s, 3 H, Me), 7.29 (d, J = 8.6 Hz, 2 H, ArH) 7.97 (d, J = 8.6 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.19, 142.50, 134.82, 131.58, 118.14, 21.37, 20.21.

4-Chloro-1-(diacetoxyiodo)benzene

Yield: 0.265 g (74.4%); mp 110-112 °C (lit.¹⁴ mp 109.8-113.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.46 (d, J = 8.6 Hz, 2 H, ArH), 8.01 (d, J = 8.6 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.30, 138.27, 136.22, 131.07, 118.68, 20.18.

1-(Diacetoxyiodo)-3-(trifluoromethyl)benzene⁸

Yield: 0.305 g (77.9%); mp 146-147 °C.

¹H NMR (300 MHz, CDCl₃) δ = 2.03 (s, 6 H, MeCO₂), 7.65 (t, J = 7.9 Hz, 1 H, ArH), 7.85 (d, J = 7.9 Hz, 1 H, ArH), 8.28 (d, J = 7.9 Hz, 1 H, ArH), 8.33 (s, 1 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.54, 138.10, 132.87 (q, J_{CF} = 33.4 Hz, CCF₃), 131.67 (q, J_{CF} = 3.7 Hz, CCF₃), 131.21, 128.39 (q, J_{CF} = 3.7 Hz, CCF₃), 122.72 (q, J_{CF} = 272.8 Hz, CCF₃).

CF₃), 120.9, 20.18.

1-(Diacetoxyiodo)-3-nitrobenzene

Yield: 0.270 g (72.9%); mp 150-152 °C (lit.¹⁴ mp 151-154.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.04 (s, 6 H, MeCO₂), 7.72 (t, J =8.1 Hz, 1 H, ArH), 8.39 (d, J =8.1 Hz, 1 H, ArH), 8.44 (d, J = 8.1 Hz, 1 H, ArH), 8.94 (s, 1 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.67, 148.47, 140.35, 131.48, 129.94, 126.24, 120.46, 20.16.

1-(Diacetoxyiodo)naphthalene⁸

Yield: 0.309 g (85.4%); mp 174-175 °C.

¹H NMR (300 MHz, CDCl₃) δ = 1.92 (s, 6 H, MeCO₂), 7.51 (t, J = 7.8 Hz, 1 H, ArH), 7.62 (t, J = 7.4 Hz, 1 H, ArH), 7.71 (t, J = 7.4 Hz, 1 H, ArH), 7.89 (d, J = 7.8 Hz, 1 H, ArH), 8.09 (d, J = 8.1 Hz, 1 H, ArH), 8.10 (d, J = 8.1 Hz, 1 H, ArH), 8.49 (d, J = 7.2 Hz, 1 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.49, 137.01, 134.33, 133.46, 131.21, 129.54, 129.20, 129.07, 127.6, 126.54, 125.27, 20.16.

1,4-Bis(diacetoxyiodo)benzene

Yield: 0.290 g (65.3%); mp 226-228 °C (lit.¹⁵ mp 220-223 °C).

¹H NMR (CDCl₃) δ = 1.96 (s, 12 H, MeCO₂), 8.23 (s, 4 H, ArH).

1-(Diacetoxyiodo)-4-fluorobenzene

Yield: 0.240 g (70.7%); mp 176.5-177.5 °C (lit.¹⁴ mp 177.0-179.8 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.15-7.21 (m, 2 H, ArH), 8.07-8.13 (d, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.35, 164.17 (d, J_{CF} = 253.7 Hz, CF), 137.45 (d, J_{CF} = 8.7 Hz, CCCC), 118.41 (d, J_{CF} = 23.0 Hz, CCF), 115.39 (d, J_{CF} = 3.7 Hz, CCCCCF), 20.18.

d. References

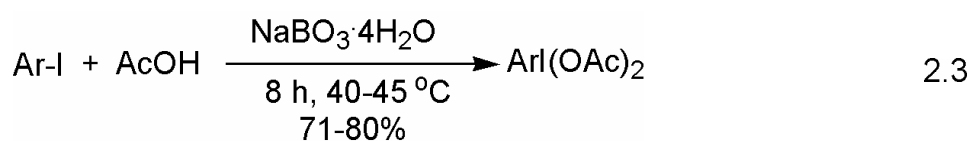
1. Willgerodt, C. Die organischen Verbindungen mit mehrwertigem Jod; Enke Verlag: Stuttgart, **1914**.
2. Reviews on (diacetoxyiodo)arenes: a) Varvoglis, A. *Chem. Soc. Rev.* **1981**, 10, 377. b) Merkushev, E. B. *Usp. Khim.* **1987**, 56, 1444; *Chem. Abstr.* **1988**, 108, 204265. c) Kirschning, A. *J. Prakt. Chem./Chem.-Ztg.* **1998**, 340, 184. d) Pohnert, G. *J. Prakt. Chem.* **2000**, 342, 731. e) Arisawa, M.; Toma, H.; Kita, Y. *Yakugaku Zasshi* **2000**, 120, 1061; *Chem. Abstr.* **2001**, 134, 29586.
3. Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*; VCH: Weinheim, **1992**.
4. Stang, P. J.; Zhdankin, V. V. *Chem. Rev.* **1996**, 96, 1123.
5. Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic press: San Diego **1997**.
6. For recent reviews on organohypervalent iodine compounds and their applications in organic synthesis: a) Kitamura, T.; Fujiwara, Y. *Org. Prep. Proced. Int.* **1997**, 29, 409. b) Varvoglis, A. *Tetrahedron* **1997**, 53, 1179. c) Muraki, T.; Togo, H.; Yokoyama, M. *Rev. Heteroatom Chem.* **1997**, 17, 213. d) Togo, H.; Hoshina, Y.; Nogami, G.; Yokoyama, M. *Yuki Gosei Kagaku Kyokaishi* **1997**, 55, 90; *Chem. Abstr.* **1997**, 126, 156952. e) Moriarty, R. M.; Prakash, O. *Adv. Heterocycl. Chem.* **1998**, 69, 1. f) Kirschning, A. *Eur. J. Org. Chem.* **1998**, 11, 2267. g) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, 54, 10927. h) Varvoglis, A.; Spyroudis, S. *Synlett* **1998**, 221. i) Ochiai, M. *Kikan Kagaku Sosetsu* **1998**, 34, 181; *Chem. Abstr.* **1998**, 129, 216196. j) Ochiai, M. *Farumashia* **1999**, 35, 140; *Chem. Abstr.* **1999**, 130, 153211. k) Kita, Y.; Egi, M.; Takada, T.; Toma, H. *Synthesis* **1999**, 885. l) Wirth, T.; Hirt, V. *Synthesis* **1999**, 1271. m) Muller, U. *Trends Photochem. Photobiol.* **1999**, 5, 117. n)

- Chemistry of Hypervalent Compounds*, Akiba, K. Ed.; Wiley-VCH: New York, **1999**. o) Grushin, V. V. *Chem. Soc. Rev.* **2000**, 29, 315. p) Ochiai, M.; Kitagawa, Y. *Yuki Gosei Kagaku Kyokaishi* **2000**, 58, 1048; *Chem. Abstr.* **2000**, 133, 362660. q) Tohma, H. *Yakugaku Zasshi* **2000**, 120, 620; *Chem. Abstr.* **2000**, 133, 222460. r) Mamaeva, E. A.; Bakibaev, A. A. *Izv. Vyssh. Uchebn.Zaved. Khim. Khim. Tekhnol.* **2000**, 43, 53; *Chem. Abstr.* **2000**, 133, 266754. s) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, 102, 2523. t) Thoma, H.; Kita, Y. *Adv. Synth. Catal.* **2004**, 346, 111. u) Thoma, H.; Kita, Y. *Yuki Gosei Kagaku Kyokaishi* **2004**, 62, 116. v) *Hypervalent Iodine Chemistry (Top. Curr. Chem.* 224); Wirth, T. Ed.; Springer-verlag, Berlin/Heidelberg, **2003**. w) Togo, H.; Sakuratani, K. *Synlett* **2002**, 1966.
7. Willgerodt, C. *Ber. Dtsch. Chem. Ges.* **1892**, 25, 3494.
8. McKillop, A.; Kemp, D. *Tetrahedron* **1989**, 45, 3299.
9. Kazmierczak, P.; Skulski, L. *Synthesis* **1998**, 1721.
10. Karele, B.; Neilands, O. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1970**, 587; *Chem. Abstr.* **1971**, 74, 42033.
11. Kazmierczak, P.; Skulski, L.; Kraszkiewicz, L. *Molecules* **2001**, 6, 881.
12. Zielinska, A.; Skulski, L. *Molecules* **2002**, 7, 806.
13. Zielinska, A.; Skulski, L. *Molecules* **2005**, 10, 190.
14. Leffler, J. E.; Story, L. J. *J. Am. Chem. Soc.* **1967**, 89, 2333.
15. Yamada, Y.; Kashima, K.; Okawara, M. *J. Polym. Sci. Polym. Lett.* **1976**, 14, 65.

B. Unexpected, Drastic Effect of Triflic Acid on Oxidative Diacetoxylation of Iodoarenes by Sodium Perborate

a. Introduction

McKillop and Kemp¹ examined the reactions of a variety of iodoarenes with sodium perborate in acetic acid at 40 °C. This method is very simple and applicable for many iodoarenes. After crystallizations, they obtained the purified products in 71-80% yields; no

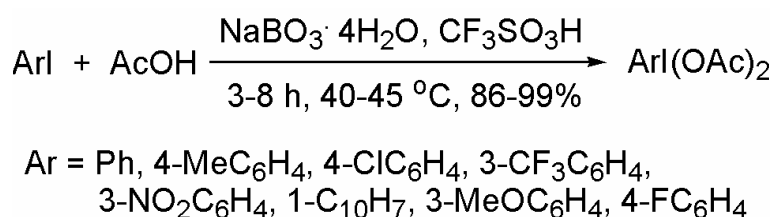


attempt was made to optimize yields. However, electron-withdrawing substituents *ortho* or *para* to the iodine inhibit this reaction, and attempts to oxidize iodobenzene in either propionic or trifluoroacetic acid were unsuccessful. The starting material was also recovered from the attempted oxidations using nitric, sulfuric or methanesulfonic acid as solvent. During the course of examination on the diacetoxylation of iodoarenes with an oxidant, triflic acid (CF₃SO₃H) added to the reaction mixture of iodoarenes and sodium perborate in acetic acid. Surprisingly a drastic increase in the yield of (diacetoxyiodo)arenes was observed. It was found that this procedure provided a facile, effective method for preparation of (diacetoxyiodo)arenes from iodoarenes. Finding of the new procedure was described here.

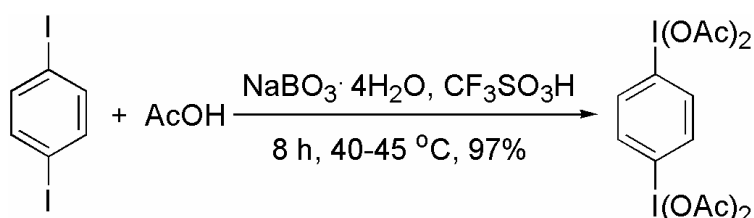
b. Results and Discussion

(Diacetoxyiodo)arenes [ArI(OAc)₂] were found in high yield within short time from the corresponding iodoarenes in AcOH, using commercial sodium perborate (NaBO₃) as an

oxidant and triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) as an additive. The results are given in Table 2.2. The oxidizing ability of NaBO_3 is much improved by addition of $\text{CF}_3\text{SO}_3\text{H}$, which is 30 times stronger than concd H_2SO_4 .² Thermal stability of $\text{CF}_3\text{SO}_3\text{H}$ is far superior to that of other acids.³ NaBO_3 is used as a strong oxidizing agent in many applications. It is a very cheap, safe, non-toxic and easily handled oxidant (stable, colorless, crystalline solid).⁴ The oxidation of iodoarenes to (diacetoxyiodo)arenes can be easily scaled up, and given the advantages of $\text{CF}_3\text{SO}_3\text{H}$ and NaBO_3 outlined above, together with the complete absence of effluent or byproduct problems. The novel method is described in Scheme 2.3.



Scheme 2.3



Scheme 2.4

The oxidative diacetoxylation reactions shown in Schemes 2.3 and 2.4 were carried out at 40-45 °C in AcOH using NaBO_3 . The presence of $\text{CF}_3\text{SO}_3\text{H}$ (in stoichiometric quantities) in the reaction mixture enhances considerably the oxidizing activity, and the purified products were obtained in 86-99% yields. When $\text{CF}_3\text{SO}_3\text{H}$ was replaced for concd H_2SO_4 , the final yields of $\text{Arl}(\text{OAc})_2$ were not improved. Table 2.2 shows that the reaction proceeds satisfactorily both with iodoarenes containing electron-donating substituents and with

iodoarenes with electron-withdrawing substituents. This method was unaffected for trisubstituted iodoarenes due to the steric effect.

Table 2.2 Preparation of (Diacetoxyiodo)arenes from Iodoarenes^a

Entry	Iodoarenes	Time (h)	Yield (%)
1	C ₆ H ₅ I	3	99
2	4-MeC ₆ H ₄ I	4	96
3	4-MeC ₆ H ₄ I	12	91 ^b
4	4-ClC ₆ H ₄ I	6	95
5	3-CF ₃ C ₆ H ₄ I	4	95
6	3-NO ₂ C ₆ H ₄ I	6	94
7	1-IC ₁₀ H ₇	7	90
8	1,4-I ₂ C ₆ H ₄ ^c	8	97
9	3-MeOC ₆ H ₄ I	4	98
10	4-FC ₆ H ₄ I	8	86

^aThe reaction of an iodoarene (1 mmol) was carried out in AcOH (9 mL) with CF₃SO₃H (6 mmol) in the presence of NaBO₃·4H₂O (10 mmol) at 40-45 °C.

^b4-Iodotoluene(10 mmol), NaBO₃·4H₂O (100 mmol), CF₃SO₃H (60 mmol), and AcOH (90 mL).

^cCH₂Cl₂ (3 mL) was added. The product was 1,4-bis(diacetoxyiodo)benzene.

The effect of CF₃SO₃H is not clear, but there are two possible explanations for the effect of CF₃SO₃H on the oxidative diacetoxylation of iodoarenes. One is the increase in solubility of NaBO₃ by adding CF₃SO₃H. On adding CF₃SO₃H, NaBO₃ is suspended, miscible in AcOH, and it becomes easy to oxidize iodoarenes. Another is that an in situ generated

(diacetoxyiodo)arene participates the oxidation of iodoarenes. The (diacetoxyiodo)benzene undergoes the ligand exchange with $\text{CF}_3\text{SO}_3\text{H}$ to probably form an $\text{ArI}(\text{OTf})_2$, which is highly reactive⁵ and can oxidize iodoarenes. Such oxidation using a reactive hypervalent iodine compound, [hydroxy(tosyloxy)iodo]benzene, has been observed to proceed under mild conditions.⁶

c. Experimental Section

Optimized Procedure for Preparing (Diacetoxyiodo)arenes from Iodoarenes

Sodium perborate tetrahydrate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$) (10 mmol) was slowly added portionwise during 10 min to a stirred solution of an iodoarene (1 mmol) in AcOH (9 mL) with $\text{CF}_3\text{SO}_3\text{H}$ (6 mmol) at 40-45 °C, and the mixture was stirred at this temperature until TLC analysis indicated completion of reaction. In the case of 1,4-diiodobenzene, dichloromethane (3 mL) was added for dissolving 1,4-diiodobenzene completely. Reaction time varied from 3 h to maximum 8 h. The solution was then concentrated to half its volume by evaporation of AcOH under reduced pressure, and H_2O (10 mL) was added. The solid separated was collected by filtration, washed with H_2O , and dried in air. A second crop of product was obtained by extraction of the filtrate with CH_2Cl_2 (3x10 mL) followed by drying of the combined extracts (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation under reduced pressure. The combined crude products were purified by recrystallization from acetic acid/hexane.

Large Scale Preparation of 1-(Diacetoxyiodo)-4-methylbenzene from 4-Iodotoluene

NaBO_3 (100 mmol) was slowly added portionwise during 20 min to a stirred solution of 4-iodotoluene (2.188 g, 10 mmol) in AcOH (90 mL) with $\text{CF}_3\text{SO}_3\text{H}$ (60 mmol) at 40-45 °C, and

the mixture was stirred at this temperature until TLC analysis indicated completion of reaction. Reaction time needed 12 h. The solution was then concentrated to half its volume by evaporation of AcOH under reduced pressure, and H₂O (100 mL) was added. The solid separated was collected by filtration, washed with H₂O and dried in air. A second crop of product was obtained by extraction of the filtrate with CH₂Cl₂ (3x100 mL) followed by drying of the combined extracts (anhydrous Na₂SO₄), filtration and removal of the solvent by evaporation under reduced pressure. The combined crude products were purified by recrystallization from acetic acid/hexane to give 3.055 g (91%) of 1-(diacetoxyiodo)-4-methylbenzene.

(Diacetoxyiodo)benzene

Yield: 0.321 g (99%); mp 162-163 °C (lit.⁷ mp 161.1-162.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 1.91 (s, 6 H, MeCO₂), 7.37-7.43 (m, 2 H, ArH), 7.48-7.54 (m, 1 H, ArH), 7.97-8.02 (m, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.4, 134.9, 131.7, 131.0, 121.5, 20.4.

1-(Diacetoxyiodo)-4-methylbenzene

Yield: 0.300 g (96%); mp 106-108 °C (lit.⁷ mp 106-110 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.00 (s, 6 H, MeCO₂), 2.44 (s, 3 H, Me), 7.29 (d, J = 8.6 Hz, 2 H, ArH), 7.97 (d, J = 8.6 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.2, 142.5, 134.8, 131.6, 118.1, 21.4, 20.2.

4-Chloro-1-(diacetoxyiodo)benzene

Yield: 0.317 g (95%); mp 110-112 °C (lit.⁷ mp 109.8-113.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.46 (d, J = 8.6 Hz, 2 H, ArH), 8.01 (d, J = 8.6 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 176.3, 138.3, 136.2, 131.1, 118.7, 20.2.

1-(Diacetoxyiodo)-3-(trifluoromethyl)benzene¹

Yield: 0.356 g (95%); mp 146-147 °C.

^1H NMR (300 MHz, CDCl_3) δ = 2.03 (s, 6 H, MeCO_2), 7.65 (t, J = 7.9 Hz, 1 H, ArH), 7.85 (d, J = 7.9 Hz, 1 H, ArH), 8.28 (d, J = 7.9 Hz, 1 H, ArH), 8.33 (s, 1 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 176.5, 138.1, 132.9 (q, J_{CF} = 33.4 Hz, CCF_3), 131.7 (q, J_{CF} = 3.7 Hz, CCCF_3), 131.2, 128.4 (q, J_{CF} = 3.7 Hz, CCCF_3), 122.7 (q, J_{CF} = 270.8 Hz, CF_3), 120.9, 20.2.

1-(Diacetoxyiodo)-3-nitrobenzene

Yield: 0.322 g (94%); mp 150-152 °C (lit.⁷ mp 151-154.2 °C).

^1H NMR (300 MHz, CDCl_3) δ = 2.04 (s, 6 H, MeCO_2), 7.72 (t, J = 8.1 Hz, 1 H, ArH), 8.38-8.45 (m, 2 H, ArH), 8.94 (s, 1 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 176.7, 148.5, 140.4, 131.5, 129.9, 126.2, 120.5, 20.2.

1-(Diacetoxyiodo)naphthalene¹

Yield: 0.311 g (90%); mp 174-175 °C.

^1H NMR (300 MHz, CDCl_3) δ = 1.92 (s, 6 H, MeCO_2), 7.51 (t, J = 7.8 Hz, 1 H, ArH), 7.62 (t, J = 7.4 Hz, 1 H, ArH), 7.71 (t, J = 7.4 Hz, 1 H, ArH), 7.89 (d, J = 7.8 Hz, 1 H, ArH), 8.09 (d, J = 8.1 Hz, 1 H, ArH), 8.10 (d, J = 8.1 Hz, 1 H, ArH), 8.49 (d, J = 7.2 Hz, 1 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 176.5, 137.0, 134.3, 133.5, 131.2, 129.5, 129.2, 129.1, 127.6, 126.5, 125.3, 20.2.

1,4-Bis(diacetoxyiodo)benzene

Yield: 0.425 g (97%); mp 226-228 °C (lit.⁸ mp 220-223 °C).

^1H NMR (300 MHz, CD_3OD) δ = 1.98 (s, 12 H, MeCO_2), 8.23 (s, 4 H, ArH).

1-(Diacetoxyiodo)-3-methoxybenzene

Yield: 0.339 g (98%); mp 132-134 °C (lit.⁹ mp 133-135 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.02 (s, 6 H, MeCO₂), 3.86 (s, 3 H, OMe), 7.11 (s, 1 H, ArH), 7.41 (t, J = 8.0 Hz, 1 H, ArH), 7.65 (d, J = 8.0 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.3, 160.3, 131.4, 126.9, 121.2, 120.3, 117.7, 55.3, 20.2.

1-(Diacetoxyiodo)-4-fluorobenzene

Yield: 0.315 g (86%); mp 176.5-177.5 °C (lit.⁷ mp 177.0-179.8 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.15-7.21 (m, 2 H, ArH), 8.07-8.13 (m, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.4, 164.2 (d, J_{CF} = 252.2 Hz, CF), 137.5 (d, J_{CF} = 8.6 Hz, CCF), 118.4 (d, J_{CF} = 22.9 Hz, CCCC), 115.4, 20.2.

d. References

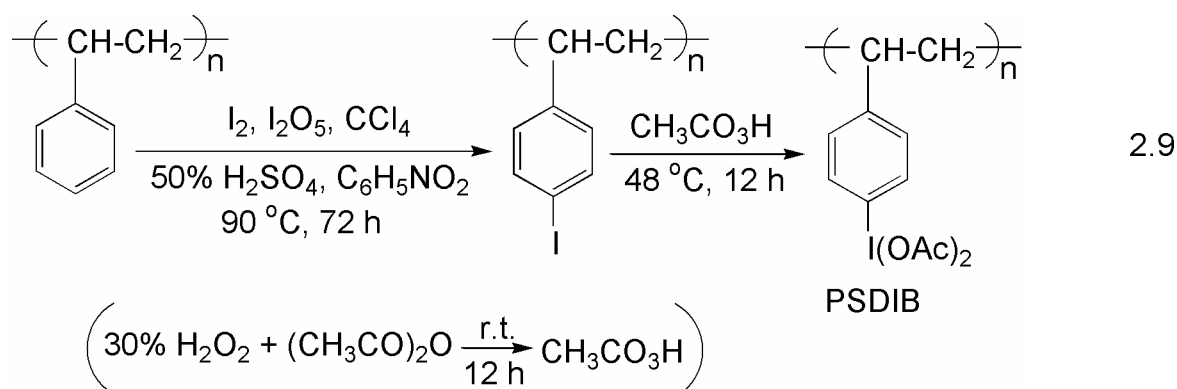
1. McKillop, A.; Kemp, D. *Tetrahedron* **1989**, 45, 3299.
2. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; 3rd Ed. Harper & Row: New York, **1987**, 280.
3. General description of triflic acid and its derivatives: *Klaus F. Meyer GmbH*
http://www.klausfmeyer.de/triflic_description.htm
4. Firouzbadi, H.; Iranpoor, N.; Amani, K. *Green Chemistry* **2001**, 3, 131.
5. Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *Synthesis* **1994**, 147.
6. Koser, G.; Wettach, R. H. *J. Org. Chem.* **1980**, 45, 1543.

7. Leffler, J. E.; Story, L. J. *J. Am. Chem. Soc.* **1967**, 89, 2333.
8. Yamada, Y.; Kashima, K.; Okawara, M. *J. Polym. Sci. Polym. Lett.* **1976**, 14, 65.
9. Kazmierczak, P.; Skulski, L.; Kraszkiewicz, L. *Molecules* **2001**, 6, 881

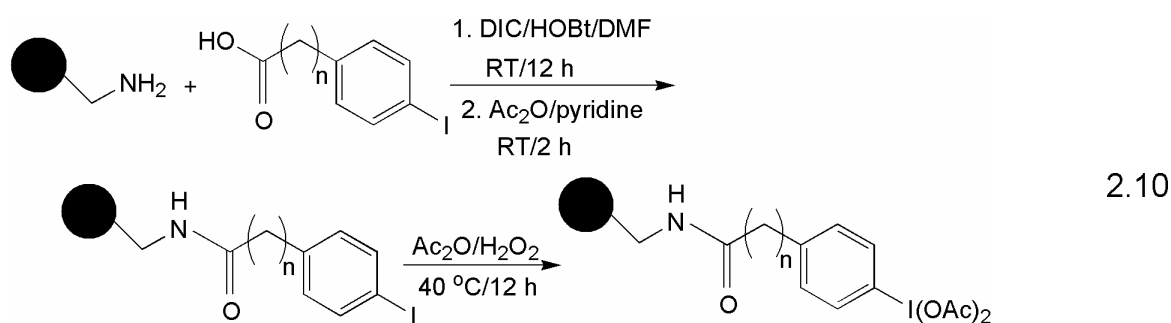
C. Alternative, Easy and Efficient Preparation of Poly[4-(Diacetoxyiodo)styrene (PSDIB) from Poly(4-iodostyrene) Using Sodium perborate as the Oxidant

a. Introduction

Several polymer-bound oxidants have been reported,¹ and polymer-supported hypervalent iodine reagents should be a welcome addition due to their versatility, low toxicity, and high reactivity. Among hypervalent iodine compounds, (diacetoxyiodo)benzene has attracted significant interest, while poly[4-(diacetoxyiodo)styrene] (PSDIB) is expected to have the same reactivity as (diacetoxyiodo)benzene.² Hitherto, PSDIB has found application in many reactions, such as the preparation of phenylpolystyryl iodonium bisulfate, 3,4-dihydro-2,1-benzothiazine 2,2-dioxides, 2,5-disubstituted oxazoles, 5-7 membered cyclic ethers, and methyl carbamates. It has also been applied to the oxidation of amines and alcohols, iodination of aromatic compounds, and the oxidative 1,2-aryl migration of alkyl aryl ketones.³ The major advantage of polymer-bound reagents is that the polymeric reagents can be regenerated and reused as an environmentally benign reagent. Preparation of the polymeric version of the iodine (III) reagent as a form of polymer-supported (diacetoxyiodo)benzene was reported by several research groups. For example, Okawara et al.⁴ showed that PSDIB could be prepared by iodination of polystyrene followed by peracetic acid oxidation (2.9).



Giannis et al.⁵ reported the preparation of aminomethylpolystyrene-supported (diacetoxyiodo)benzene (2.10).



Ko et al.⁶ synthesized Merrifield's peptide polymer-supported (diacetoxyiodo)benzene from Merrifield's peptide resin (2.11).

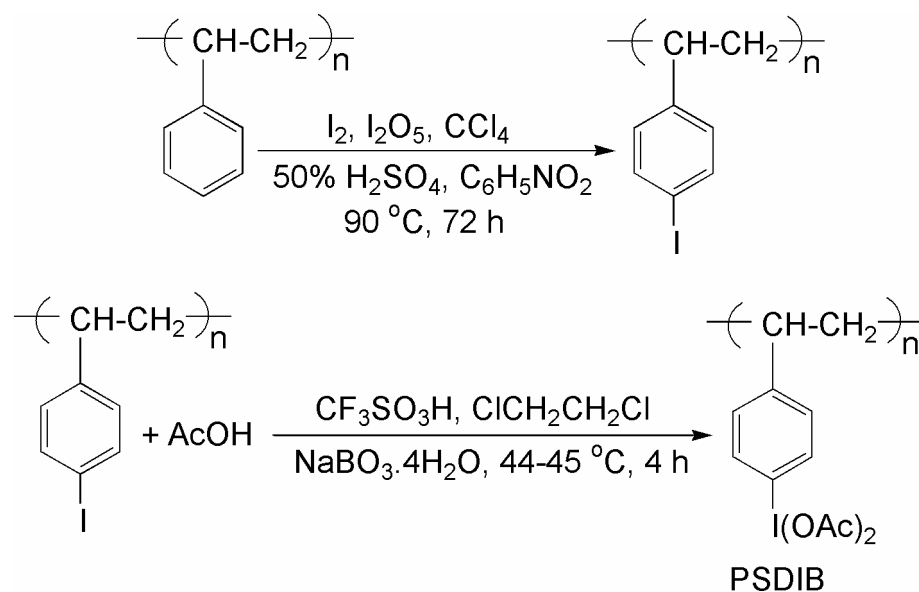


The standard and most general method for the synthesis of poly[4-(diacetoxyiodo)styrene]

(PSDIB) is the oxidative diacetoxylation of poly(4-iodostyrene) by peracetic acid at room temperature or 48 °C,^{2a,3s,4} however, it requires prolonged reaction times (15-24 h). Aminomethylated polystyrene is inexpensive and commercially available prefunctionalized polymers for the preparation of aminomethyl polystyrene-supported (diacetoxyiodo)benzene,⁵ which should be protected from direct sunlight and can be stored in a refrigerator although no appreciable decomposition was observed at room temperature. The activity of Merrifield's peptide-supported (diacetoxyiodo)benzene was found to be 1.4 mmol/g.⁶ The oxidation of Hantzsch 1,4-dihydropyridines with Merrifield's peptide-supported (diacetoxyiodo)benzene afforded good yields but the presence of electron-withdrawing groups such as nitro group retarded the oxidation. In order to circumvent these problems, an alternative method for the preparation of PSDIB from poly(4-iodostyrene) using sodium perborate was envisaged.⁷

b. Results and Discussion

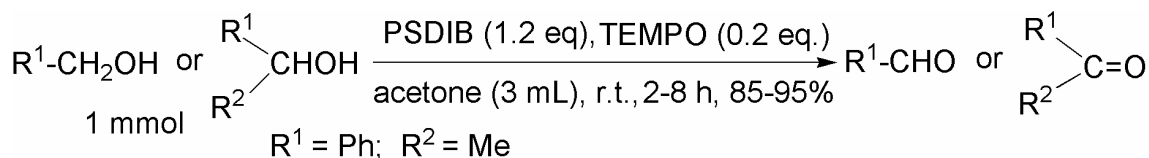
Poly[4-(diacetoxyiodo)styrene] (PSDIB) was prepared from the corresponding poly(4-iodostyrene) in AcOH and 1,2-dichloroethane using commercial sodium perborate as an oxidant and triflic acid as an additive at 44-45 °C (Scheme 2.5). After filtration, PSDIB was washed with diethyl ether and dried. Poly(4-iodostyrene) was prepared by the reaction of polystyrene with iodine, iodine pentaoxide, carbon tetrachloride, and sulfuric acid (50%) in nitrobenzene at 90 °C for 72 h.^{3d} The oxidizing ability of NaBO₃ is much improved by addition of CF₃SO₃H. The polymer loading of PSDIB in terms of the (diacetoxyiodo)phenyl group was determined by iodometric titration⁸ to be 1.86 mmol/g. When triflic acid was replaced with concentrated sulfuric acid, the activity of PSDIB was not improved.



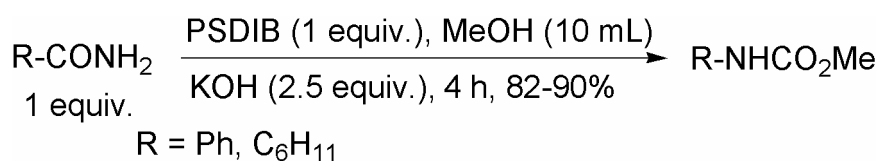
Scheme 2.5

In order to test their activity, benzyl alcohol was converted to benzaldehyde, after a short reaction time, with a defined quantity of PSDIB. The yield of benzaldehyde (Table 2.3) was about the same as that reported in the literature.^{3f} Subsequently, several other substrates, 1-phenylethanol, benzamide, cyclohexanecarboxamide, and propiophenone, were converted to acetophenone, methyl *N*-phenylcarbamate, methyl *N*-cyclohexylcarbamate, and methyl 2-phenylpropionate, respectively (Scheme 2.6, 2.7, 2.8), with short reaction times in excellent yields (Table 2.3).^{3f-h}

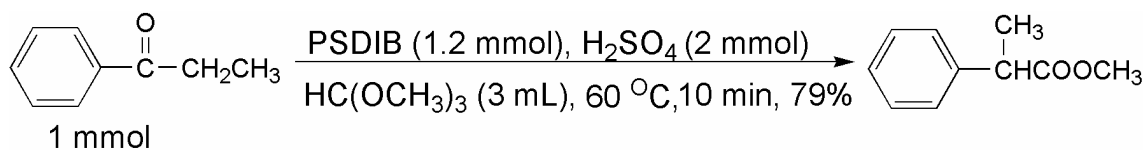
The regeneration and recycling of the used PSDIB was also studied. After the first run, the polymer was recovered by filtration, washed with methanol, and the recovered polymer was then reoxidized with sodium perborate in the usual manner. The activity of regenerated PSDIB was found to be 1.63 mmol/g by iodometric titration. Oxidation of 1-phenylethanol with the regenerated PSDIB under the same reaction conditions gave acetophenone in 90% yield.



Scheme 2.6



Scheme 2.7



Scheme 2.8

Table 2.3 Oxidation of Alcohols, Carboxamides and Propiophenone Using PSDIB

Entry	Reagent	Product	Time (h)	Yield (%)
1	Benzyl alcohol	Benzaldehyde ^a	2	85
2	1-Phenylethanol	Acetophenone ^a	8	95
3	Benzamide	Methyl <i>N</i> -Phenylcarbamate ^b	12	90
4	Cyclohexanecarboxamide	Methyl <i>N</i> -Cyclohexylcarbamate ^b	4	82
5	Propiophenone	Methyl 2-Phenylpropionate ^c	10 min	80

^aAlcohol (1 mmol), TEMPO (31 mg, 0.2 mmol), Me₂CO (3 mL), PSDIB (0.64 g, 1.2 mmol), r.t.

^bKOH (2.5 equiv.), MeOH (10 mL), carboxamide (1 equiv.), PSDIB (0.54 g, 1 equiv.), 5-10 °C to r.t.

^cH₂SO₄ (2 mmol), propiophenone (1 mmol), HC(OMe)₃ (3 mL), PSDIB (0.64 g, 1.2 mmol), 60 °C.

c. Experimental Section

Preparation of Poly(4-iodostyrene)^{3d}

A mixture of polystyrene (5 g, 47.81 mmol), I₂ (5.62 g, 22.19 mmol), I₂O₅ (2.19 g, 6.56 mmol), CCl₄ (12.5 mL), H₂SO₄ (50%, 10.9 mL) and nitrobenzene (62.5 mL) was kept at 90 °C for 72 h. After the reaction was complete, the reaction mixture was diluted with CHCl₃ (32 mL), then MeOH (469 mL) was added, and a precipitate formed. The precipitate was collected by filtration; yield, 5.80 g.

IR (KBr): 3050, 3023, 2919, 2749, 1524, 1482, 1003. 818, 757, 699, 538 cm⁻¹

Preparation of Poly[4-(diacetoxyiodo)styrene] (PSDIB)

A solution of poly(4-iodostyrene) (0.231 g), AcOH (5 mL), ClCH₂CH₂Cl (7 mL), and TfOH (6 mmol) was heated with stirring at 44-45 °C. Then, NaBO₃·4H₂O (6 mmol) was added slowly portionwise over 10 min and stirring was continued for 4 h. The solution was then concentrated by evaporation of ClCH₂CH₂Cl and AcOH under reduced pressure, water (10 mL) was added, The precipitate was collected by filtration, washed with H₂O (10 mL), Et₂O (20 mL), and dried; yield, 0.275 g.

A large-scale synthesis of PSDIB was conducted in a similar manner. A solution of poly(4-iodostyrene) (1.38 g) in a mixture of AcOH (30 mL), ClCH₂CH₂Cl (50 mL), and TfOH (36 mmol) was heated 44-45 °C with stirring. Then, NaBO₃·4H₂O (36 mmol) was added portionwise over 20 min and the stirring was continued for 4 h. Workup as above gave

PSDIB; yield, 1.62 g.

IR (KBr): 3055, 3018, 2923, 2848, 1628 (br), 1581 (br), 1483, 1450, 1406, 1274, 1172, 1029, 1005, 819, 762, 702, 640, 540 cm^{-1}

Iodometric Titration⁸

Deionized water (12.5 mL), H_2SO_4 (6 N, 1.25 mL), KI (0.25 g), CHCl_3 (1.25 mL), and finally the prepared PSDIB (0.0310 g) were placed in a 100-mL round-bottom flask, the mixture was stirred for 4 h, and then titrated against $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 N). The polymer loading of the (diacetoxyiodo)phenyl group was calculated to be 1.86 mmol/g.

Oxidation of Alcohols with PSDIB; General Procedure

PSDIB (0.64 g, 1.2 mmol) was added to a solution of alcohol (1 mmol) and TEMPO (31 mg, 0.2 mmol) in acetone (3 mL) and the mixture was stirred at room temperature for the time given in Table 2.3. At end of the reaction, Et_2O (10 mL) was added and the mixture was filtered to remove the polymer. After removal of the solvent, the filtrate was poured into H_2O (10 mL) and extracted with Et_2O (3×10 mL). The combined organic layer was dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was chromatographed (silica gel) to give the pure carbonyl product.

Benzaldehyde

Yield: 0.095 g (85%).

^1H NMR (300 MHz, CDCl_3) δ = (t, J = 7.5 Hz 1 H, ArH), 7.63 (t, J = 7.5 Hz 2 H, ArH), 7.89 (d, J = 7.5 Hz, 2 H, ArH), 10.02 (s, 1H, CHO).

^{13}C NMR (75 MHz, CDCl_3) δ = 192.33, 136.42, 134.43, 129.72, 128.98.

Acetophenone

Yield: 0.127 g (95%).

^1H NMR (300 MHz, CDCl_3) δ = 2.60 (s, 3 H, MeCO), 7.46 (t, J = 7.5 Hz 1 H, ArH), 7.55 (t, J = 7.5 Hz 2 H, ArH), 7.95 (d, J = 7.5 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 198.04, 137.09, 133.01, 128.48, 128.22, 26.50.

Substituted Methyl Carbamates; General Procedure

To a stirred solution of KOH (2.5 equiv.) in MeOH (10 mL) was added carboxamide (1 equiv.). The mixture was stirred at room temperature until a homogeneous solution was obtained and then the solution was cooled to $-10\text{ }^\circ\text{C}$ in an ice-water bath. PSDIB (0.54 g, 1 equiv.) was added in one portion and dissolved within 5 min to give a clear yellow solution. The reaction was stirred at ice-bath temperature for 15 min and then warmed to room temperature with stirring for an additional 4 h. Upon completion of the reaction (TLC), MeOH was removed in vacuo, the yellow residue was poured into H_2O (10 mL), and extracted with CH_2Cl_2 ($3\times 10\text{ mL}$). The CH_2Cl_2 extracts were combined, washed with H_2O (10 mL) and brine (10 mL), dried over anhyd Na_2SO_4 , and filtered. The CH_2Cl_2 was removed in vacuo to give the crude carbamate, which was purified by flash column chromatography (silica gel) to afford the pure final product.

Methyl *N*-Phenylcarbamate

Yield: 0.142 g (90%); mp $46\text{--}47\text{ }^\circ\text{C}$ (lit.⁹ mp $48\text{--}49\text{ }^\circ\text{C}$).

^1H NMR (300 MHz, CDCl_3) δ = 3.76 (s, 3 H, OCH_3), 6.80 (br s, 1 H, NH), 7.05 (t, J = 8 Hz 1 H, ArH), 7.29 (t, J = 8 Hz 2 H, ArH), 7.37 (d, J = 8 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 154.09, 137.82, 128.96, 123.40, 118.74, 52.25.

Methyl *N*-Cyclohexylcarbamate

Yield: 0.130 g (82%); mp $72\text{--}73\text{ }^\circ\text{C}$ (lit.¹⁰ mp $76\text{--}78\text{ }^\circ\text{C}$).

^1H NMR (300 MHz, CDCl_3) δ = 1.01–1.86 (m, 10 H, C_6H_{11}), 3.38 (br s, 1 H, C_6H_{11}), 3.57 (s,

3 H, OCH₃), 4.81 (br s, 1 H, NH).

¹³C NMR (75 MHz, CDCl₃) δ = 156.13, 51.52, 49.66, 33.20, 25.30, 24.63.

Methyl 2-Phenylpropionate^{3h}

H₂SO₄ (2 mmol) was added dropwise to a stirred solution of PSDIB (0.64 g, 1.2 mmol) and propiophenone (1 mmol) in trimethylorthoformate (3 mL) at room temperature. The reaction mixture was stirred at 60 °C for 10 min, quenched with H₂O (10 mL) and extracted with Et₂O (3×10 mL). The combined organic layer was dried (Na₂SO₄), filtered, and the solvent was removed in vacuo. The residue was chromatographed (silica gel) to give the pure methyl 2-phenylpropionate.

Methyl 2-Phenylpropionate

Yield: 0.142 g (79.5%).

¹H NMR (300 MHz, CDCl₃) δ = 1.49 (d, J = 7.0 Hz 3 H, Me), 3.64 (s, 3 H, OMe), 3.72 (q, J = 7.0 Hz, 1 H, CHMe), 7.29 (s, 5 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 174.92, 140.52, 128.56, 127.41, 127.07, 51.92, 45.37, 18.53.

Purification of Recovered Poly(iodostyrene)

Recovered poly(iodostyrene) (2.5 g) was dissolved in CHCl₃ (42 mL) at 60 °C, then MeOH was added to precipitate the poly(iodostyrene). After filtration, 1.9 g pure poly(iodostyrene) was obtained.

Regeneration of Poly[4-(diacetoxyiodo)styrene] (PSDIB)

Mixture of poly(4-iodostyrene) (1.8 g), AcOH (39 mL), 1,2-dichloroethane (65 mL), and TfOH (46 mmol) was heated with stirring at 44-45 °C, then NaBO₃·4H₂O (46 mmol) was added portionwise over 20 min and stirring was continued for 8 h. Workup of the reaction mixture gave 2.1 g product. The loading rate of (diacetoxyiodo)phenyl group was found 1.63

mmol/g (iodometric titration).

Oxidation of 1-Phenylethanol with Regenerated PSDIB

Regenerated PSDIB (0.73 g, 1.2 mmol) was added to a solution of 1-Phenylethanol (1 mmol), and TEMPO (31 mg, 0.2 mmol) in acetone (3 mL) and the mixture was stirred at room temperature for 12 h. After reaction, Et₂O (10 mL) was added and the mixture was filtered to remove the polymer. The filtrate was poured into H₂O (10 mL) and extracted with Et₂O (3×10 mL). The combined organic layers were dried (Na₂SO₄), filtered, and the solvent was removed in vacuo. The residue was chromatographed (silica gel) to give the pure acetophenone (90%).

d. References

1. a) Goudarzian, N.; Ghahramani, P.; Hossini, S. *Polym. Int.* **1996**, 39, 61. b) Lee, R. A.; Donald, D. S. *Tetrahedron Lett.* **1997**, 38, 3857. c) Hinzen, B.; Ley, S. V. *J. Chem. Soc. Perkin Trans. I* **1997**, 13, 1907. d) Harris, J. M.; Liu, Y.; Chai, S.; Andrews, M. D.; Vederas, J. C. *J. Org. Chem.* **1998**, 63, 2407. e) Abraham, S.; Rajan, P. K.; Sreekumar, K. *Polym. Int.* **1998**, 45, 271. f) Habermann, J.; Ley, S. V.; Scott, J. S. *J. Chem. Soc. Perkin Trans. I* **1999**, 1253.
2. a) Togo, H.; Nogami, G.; Yokoyama, M. *Synlett* **1998**, 5, 534. b) Ley, S. V.; Thomas, A. W.; Finch, H. *J. Chem. Soc. Perkin Trans. I* **1999**, 6, 669. c) Ley, S. V.; Schucht, O.; Thomas, A. W.; Murray, P. J. *J. Chem. Soc. Perkin Trans. I* **1999**, 1251.
3. a) Yamada, Y.; Okawara, M. *Die Makromol. Chem.* **1972**, 152, 153. b) Hallensleben, M. L. *Angew. Makromol. Chem.* **1972**, 27, 223. c) Zupan, M.; Pollak, A. *J. Chem. Soc. Chem. Commun.* **1975**, 715. d) Sakuratani, K.; Togo, H. *ARKIVOC* **2003**, vi, 11. e) Huang, X.; Chen,

- J.-M. *Chin. J. Chem.* **2004**, 22, 222. f) Sakuratani, K.; Togo, H. *Synthesis* **2003**, 21. g) Moriarty, R. M.; Chany II, C. J.; Vaid, R. K.; Prakash, O.; Tuladhar, S. M. *J. Org. Chem.* **1993**, 58, 2478. h) Tamura, Y.; Yakura, T.; Shirouchi, Y.; Haruta, J. *Chem. Pharm. Bull.* **1985**, 33, 1097. i) Kawamura, Y.; Maruyama, M.; Tokuoka, T.; Tsukayama, M. *Synthesis* **2002**, 2490. j) Cheng, D.; Chen, Z. *Synth. Commun.* **2002**, 32, 2155. k) Chen, D.; Chen, Z. *Synth. Commun.* **2001**, 31, 421. l) Huang, X.; Zhu, Q. *Synth Commun.* **2001**, 31, 111. m) Jonathan, H. J.; Rath, N. P.; Spilling, C. D. *J. Org. Chem.* **2005**, 70, 6398. n) Sheng, S.; Zhong, M.; Liu, X.; Luo, Q.; Chen, H. *J. Chem. Res.* **2004**, 392. o) Cheng, D.; Chen, Z.; Zheng, Q. *Synth. Commun.* **2003**, 33, 2671. p) Tohma, H.; Maegawa, T.; Kita, Y. *Synlett* **2003**, 5, 723. q) Tohma, H.; Maegawa, T.; Takizawa, S.; Kita, Y. *Adv. Synth. Catal.* **2002**, 344, 328. r) Tohma, H.; Takizawa, S.; Maegawa, T.; Kita, Y. *Angew. Chem.* **2000**, 39, 1306. s) Wang, G.; Chen, Z. *Synth. Commun.* **1999**, 29, 2859. t) Yamada, K.; Urakawa, H.; Oku, H.; Katakai, R. *J. Peptide Res.* **2004**, 64, 43. u) Liu, S.; Zhang, J.; Tian, G.; Liu, P. *Synth. Commun.* **2005**, 35, 1753. v) Teduka, T.; Togo, H. *Synlett* **2005**, 6, 923. w) Abo, T.; Sawaguchi, M.; Senboku, H.; Hara, S. *Molecules* **2005**, 10, 183. x) Okawara, M.; Kurusu, Y.; Imoto, E. *Kogyo Kagaku Zasshi* **1962**, 65, 816; *Chem. Abstr.* **1962**, 58, 3477. y) Boehlow, T. R.; Harburn, J. J.; Spilling, C. D. *J. Org. Chem.* **2001**, 66, 3111.
4. Okawara, M.; Mizuta, K. *Kogyo Kagaku Zasshi* [J. Chem. Soc. Japan, Ind. Chem. Sect.] **1961**, 64, 232.
5. Ficht, S.; Mulbaier, M.; Giannis, A. *Tetrahedron* **2001**, 57, 4863.
6. Lee, J.; Ko, K. *Bull. Korean Chem. Soc.* **2004**, 25, 19.
7. Hossain, M. D.; Kitamura, T. *J. Org. Chem.* **2005**, 70, 6984.
8. Lucas, H. J.; Kennedy, E. R.; Formo, M. W. *Org. Synth.* **1942**, 22, 70.

9. George, D. K.; Moore, D. H.; Brian, W. P.; Garman, J. A. *J. Agric. Food Chem.* **1954**, *2*, 356.
10. Curini, M.; Epifano, F.; Maltese, F.; Rosati, O. *Tetrahedron Lett.* **2002**, *43*, 4895.

D. Direct, Easy, and Scalable Preparation of (Diacetoxyiodo)arenes from Arenes Using Potassium Peroxodisulfate as the Oxidant

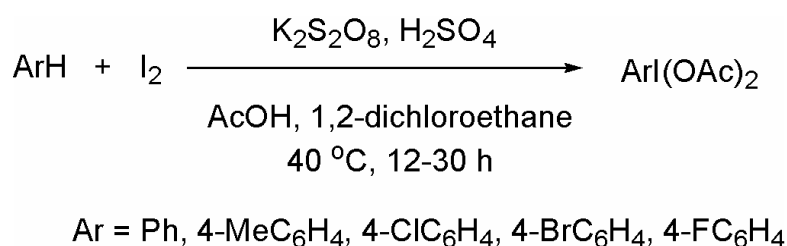
a. Introduction

In most of the previous methods, iodobenzene is used as a starting material to prepare (diacetoxyiodo)benzene. Iodobenzene is readily available but expensive. The most ideal procedure for (diacetoxyiodo)benzene should involve a straightforward synthesis from benzene and iodine. This procedure gives a direct and efficient method that does not contain the step via iodobenzene synthesis. Probably, there are no methods available for preparing (diacetoxyiodo)benzene directly from benzene and iodine. Very recently, Shreeve and co-workers reported a direct synthesis of (diacetoxyiodo)arenes mediated by Selectfluor.¹ In the Selectfluor-mediated method, electron-rich di- and tri-substituted benzenes were used as starting materials to obtain the corresponding $\text{ArI}(\text{OAc})_2$ in good yields. However, it seems that this method cannot be applied for benzene, mono-substituted benzenes, and electron-deficient arenes, judging from the Selectfluor-mediated iodination of arenes.² During the course of systematic studies on effective and easy preparations of $\text{ArI}(\text{OAc})_2$, two methods for their synthesis from iodoarenes have already devised.³ Herein, a direct, easy method for the preparation of (diacetoxyiodo)benzene from benzene has been reported. Also the application to toluene and less reactive halobenzenes were described.

b. Results and Discussion

A direct and efficient method for preparing $\text{ArI}(\text{OAc})_2$ were generated in good yield from

the corresponding arenes with iodine in AcOH, using commercial potassium peroxodisulfate, $K_2S_2O_8$, as the oxidant. The results are given in Table 2.4. Addition of concd H_2SO_4 is essential to generate (diacetoxyiodo)arenes. Trifluoromethanesulfonic acid was also effective but H_2SO_4 was convenient for handling and workup. The oxidation of arenes to (diacetoxyiodo)arenes can be easily scaled up, and given the advantages of $K_2S_2O_8$ outlined above, together with the complete absence of effluent or byproduct problems. The novel method is described in Scheme 2.9.



Scheme 2.9

Table 2.4 Direct Synthesis of (Diacetoxyiodo)arenes from Arenes^a

Entry	Arene	Time (h)	Product	Yield (%)
1	Benzene	20	PhI(OAc) ₂	73
2 ^b	Benzene	24	PhI(OAc) ₂	70
3 ^c	Benzene	28	PhI(OAc) ₂	66
4 ^d	Benzene	30	PhI(OAc) ₂	64
5	Toluene	12	4-MeC ₆ H ₄ I(OAc) ₂	70
6	Chlorobenzene	20	4-ClC ₆ H ₄ I(OAc) ₂	71
7	Bromobenzene	20	4-BrC ₆ H ₄ I(OAc) ₂	70
8	Fluorobenzene	20	4-FC ₆ H ₄ I(OAc) ₂	69

^aThe reaction of an arene (1.18 mmol) was carried out in AcOH (5 mL), I_2 (0.5 mmol), 1,2-

dichloroethane (2 mL), and H₂SO₄ (4 mmol) in the presence of K₂S₂O₈ (5 mmol) at 40 °C.

^bBenzene (1.18 mmol), AcOH (2 mL), I₂ (0.5 mmol), 1,2-dichloroethane (2 mL), H₂SO₄ (4 mmol), and K₂S₂O₈ (5 mmol).

^cBenzene (11.8 mmol), AcOH (20 mL), I₂ (5 mmol), 1,2-dichloroethane (20 mL), H₂SO₄ (40 mmol) and K₂S₂O₈ (50 mmol).

^dBenzene (59.0 mmol), AcOH (100 mL), I₂ (25 mmol), 1,2-dichloroethane (100 mL), H₂SO₄ (200 mmol), and K₂S₂O₈ (250 mmol).

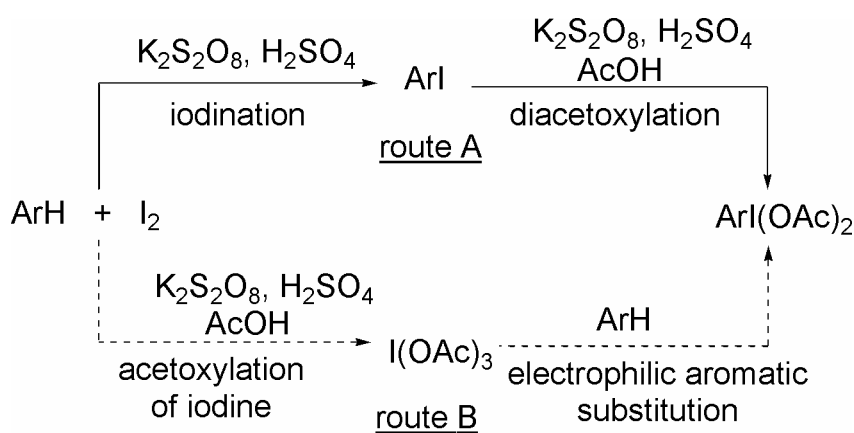
The oxidative reactions shown in Scheme 2.9 were carried out at 40 °C, in a mixture of AcOH, 1,2-dichloroethane, iodine and concd H₂SO₄. The presence of K₂S₂O₈ (in stoichiometric quantities) in the reaction mixture was indispensable because without its addition the oxidation reactions did not proceed. When K₂S₂O₈ was replaced for sodium peroxodisulfate, Na₂S₂O₈, the final yields of ArI(OAc)₂ were lowered by ca.20-25%. Attempt to use NaBO₃ for this preparation was unsuccessful. Decrease in the amount of AcOH did not affect the yield of (diacetoxyiodo)benzene. The reaction of 10- or 50-fold scale to that in entry 2 did not lead to the decrease in the yield (Table 2.4, entries 3 and 4). Toluene also gave 4-(diacetoxyiodo)toluene in good yield. Arenes bearing weakly deactivated groups such as chloro, bromo, and fluoro groups gave (diacetoxyiodo)arenes in good yields. In order to broaden the scope of this reaction, the oxidation of xylene, mesitylene, and *tert*-butylbenzene were conducted. Actually these substrates underwent the oxidation reaction. However, these reactions resulted in the formation of iodosylbenzene derivatives, respectively. Therefore, it is considered that relatively electron-rich property of these compounds causes hydrolysis of (diacetoxyiodo)arenes during the reaction or the workup procedure. This method was not applicable for arenes with strong electron-donating groups. For example, naphthalene and anisoles were quickly oxidized in the reaction mixtures, but the reaction resulted in the

decomposition and the formation of tarry products. This method was also unaffected for arenes with strong electron-withdrawing groups such as trifluoromethyl and nitro groups due to their decreased reactivity.

Mechanistically, there are two possible routes for generating (diacetoxyiodo)arenes, as shown in Scheme 2.10:

Route A: iodination of arenes, followed by diacetoxylation leading to (diacetoxyiodo)arenes;

Route B: generation of triacetoxyiodine(III), followed by electrophilic aromatic substitution to give (diacetoxyiodo)arenes.



Scheme 2.10

The latter route may be suitable because $\text{I}(\text{OAc})_3$ is a reactive electrophile and reacts with aromatics. According to the Shreeve's result,¹ $\text{I}(\text{OAc})_3$ is only effective for tri-substituted electron-rich aromatics such as mesitylene and 1-*tert*-butyl-3,5-dimethylbenzene. However, the above method is effective for benzene and electron-deficient, less reactive halobenzenes. Therefore, a plausible route is the former one.

In order to detect the intermediate iodoarene in route A, the reaction was examined with a less amount of $\text{K}_2\text{S}_2\text{O}_8$. When benzene was reacted with iodine in the presence of 2 equivalents of $\text{K}_2\text{S}_2\text{O}_8$ under the same conditions, iodobenzene was formed in 66% yield, together with 21%

yield of $\text{PhI}(\text{OAc})_2$. It was already obtained that the reaction of iodobenzene with $\text{K}_2\text{S}_2\text{O}_8/\text{H}_2\text{SO}_4$ in AcOH effectively proceeds to give (diacetoxyiodo)benzene. Therefore, it is considered that, once iodoarenes are formed, they are immediately oxidized to give $\text{ArI}(\text{OAc})_2$ under the reaction conditions.

c. Experimental Section

(Diacetoxyiodo)arenes from Arenes; General Procedure

A solution of an appropriate arene (1.18 mmol) in a mixture of AcOH (5 mL), 1,2-dichloroethane (2 mL), concd H_2SO_4 (4 mmol), and I_2 (0.5 mmol) was heated with stirring to 40 °C for 15 min. Next $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol) was added portionwise during 10 min and the stirring was continued until TLC analysis indicated completion of reaction. The reaction needed 12-30 h. After the reaction was completed, water (10 mL) was added. The precipitated solid was collected by filtration under reduced pressure, washed with CH_2Cl_2 (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with dichloromethane (3×10 mL) and finally washed with H_2O (10 mL) followed by drying (anhydrous Na_2SO_4), filtration and removal of the solvent by evaporation under reduced pressure. The crude product was purified by washing with hexane (20 mL) or recrystallized from AcOH.

(Diacetoxyiodo)benzene; Large Scale

Large scale synthesis was conducted for (diacetoxyiodo)benzene in a similar manner. A solution of benzene (4.62 g, 59 mmol) in a mixture of AcOH (100 mL), 1,2-dichloroethane (100 mL), concd H_2SO_4 (200 mmol) and I_2 (6.34g, 25 mmol) was heated with stirring to 40 °C for 20 min. Next $\text{K}_2\text{S}_2\text{O}_8$ (250 mmol) was added portionwise over 20 min and the stirring was continued for 30 h. Workup of the reaction mixture gave the purified product (10.79 g, 64%).

(Diacetoxyiodo)benzene

Yield: 0.244 g (73%); mp 160-161 °C (lit.⁴ mp 161.1-162.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.51 (t, J = 7.5 Hz, 2 H, ArH), 7.59 (t, J = 7.5 Hz, 2 H, ArH), 8.09 (d, J = 7.5 Hz, 1 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.27, 134.81, 131.61, 130.83, 121.50, 20.21.

1-(Diacetoxyiodo)-4-methylbenzene

Yield: 0.246 g (70%); mp 104-106 °C (lit.⁴ mp 106-110 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.27 (s, 6 H, MeCO₂), 2.49 (s, 3 H, Me), 7.09 (d, J = 7.8 Hz, 2 H, ArH) 7.83 (d, J = 7.8 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.36, 142.06, 135.01, 132.25, 111.72, 21.29, 20.36.

4-Chloro-1-(diacetoxyiodo)benzene

Yield: 0.263 g (71%); mp 109-110 °C (lit.⁴ mp 109.8-113.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 1.94 (s, 6 H, MeCO₂), 7.57 (d, J = 8.7 Hz, 2 H, ArH), 8.06 (d, J = 8.7 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.38, 138.34, 136.25, 131.12, 118.74, 20.22.

4-Bromo-1-(diacetoxyiodo)benzene

Yield: 0.290 g (70%); mp 108-110 °C (lit.⁴ mp 109.8-113.2 °C).

¹H NMR (300 MHz, CDCl₃) δ = 1.94 (s, 6 H, MeCO₂), 7.71 (d, J = 8.4 Hz, 2 H, ArH), 8.00 (d, J = 8.4 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 176.37, 136.33, 134.03, 126.66, 119.49, 20.22.

1-(Diacetoxyiodo)-4-fluorobenzene

Yield: 0.242 g (69%); mp 176-177 °C (lit.⁴ mp 177.0-179.8 °C).

¹H NMR (300 MHz, CDCl₃) δ = 2.01 (s, 6 H, MeCO₂), 7.15-7.27 (m, 2 H, ArH), 8.06-8.11 (m,

2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 176.39, 164.17 (d, J_{CF} = 252.82 Hz, CF), 137.46 (d, J_{CF} = 8.7 Hz, CCF), 118.41 (d, J_{CF} = 23.0 Hz, CCCC), 115.40 (d, J_{CF} = 3.7 Hz, CCCCC), 20.17.

d. References

1. Ye, C.; Twamley, B.; Shreeve, J. M. *Org. Lett.* **2005**, 7, 3961.
2. a) Zupan, M.; Iskra, J.; Stavber, S. *Tetrahedron Lett.* **1997**, 38, 6305. b) Stavber, S.; Kralj, P.; Zupan, M. *Synlett* **2002**, 598. c) Stavber, S.; Kralj, P.; Zupan, M. *Synthesis* **2002**, 1513. d) Stavber, S.; Jereb, M. *Chem. Commun.* **2002**, 488.
3. a) Hossain, M. D.; Kitamura, T. *Synthesis* **2005**, 1932. b) Hossain, M. D.; Kitamura, T. *J. Org. Chem.* **2005**, 70, 6984.
4. Leffler, J. E.; Story, L. J. *J. Am. Chem. Soc.* **1967**, 89, 2333.

Chapter III

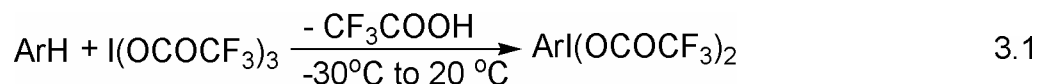
Easy Preparation of [Bis(trifluoroacetoxy)iodo]arenes from

Iodoarenes Using Potassium Peroxodisulfate as the Oxidant

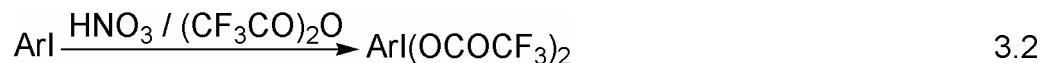
a. Introduction

[Bis(trifluoroacetoxy)iodo]arenes, $\text{ArI}(\text{OCOCF}_3)_2$, are fundamental reagents, potent and often chemoselective oxidants, widely used in modern organic synthesis. They are also used for facile transformations of alkynes, ketones, and sulfur compounds, phenolic oxidation, oxidation of nitrogen compounds, oxidative biaryl coupling, etc.¹ Several methods are available for the preparation of $\text{ArI}(\text{OCOCF}_3)_2$.

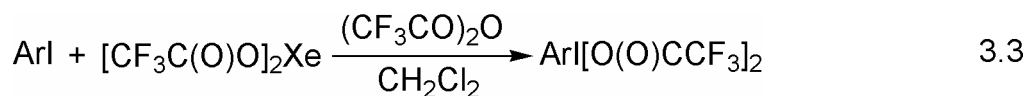
The reaction of tris(trifluoroacetoxy)iodine with arenes is the most widespread method to synthesize $\text{ArI}(\text{OCOCF}_3)_2$.²



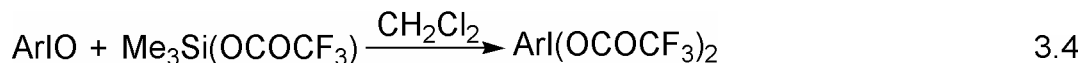
$\text{ArI}(\text{OCOCF}_3)_2$ were prepared by treating iodoarenes with HNO_3 and $(\text{F}_3\text{CCO})_2\text{O}$.³



Xenon bis(trifluoroacetate) reacted with aryl iodides in the presence of $(\text{F}_3\text{CCO})_2\text{O}$ in CH_2Cl_2 under mild condition yielding $\text{ArI}(\text{OCOCF}_3)_2$.⁴



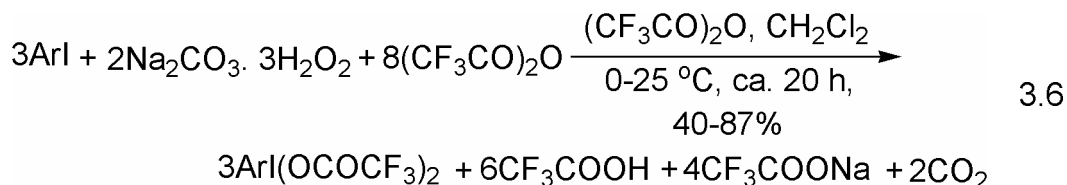
Iodosylarenes can be easily transformed into $\text{ArI}(\text{OCOCF}_3)_2$ under mild, aprotic conditions by the action of $\text{Me}_3\text{Si}(\text{OCOCF}_3)$ in CH_2Cl_2 .⁵



$\text{ArI}(\text{OCOCF}_3)_2$ is prepared by dissolving with heating (diacetoxyiodo)arenes in CF_3COOH .⁶



Preparations of the nearly pure $\text{ArI}(\text{OCOCF}_3)_2$ from some iodoarenes are reported, using $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2 / (\text{F}_3\text{CCO})_2\text{O} / \text{CH}_2\text{Cl}_2$ system.⁷



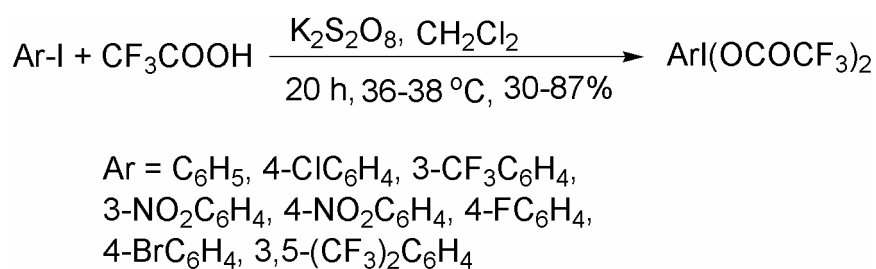
The most general synthetic method of $\text{ArI}(\text{OCOCF}_3)_2$ for laboratory use is to dissolve (diacetoxyiodo)arenes in CF_3COOH with heating.⁶ However, there is yet room for improvement in this method because contamination with (diacetoxyiodo)arenes decreases the yields. In the reaction of $\text{I}(\text{OCOCF}_3)_3$ with arenes,² the reactivity of the arenes decreases in the order: $p\text{-Me}_2\text{C}_6\text{H}_4 > \text{MePh} > \text{PhH} > \text{PhCl} > \text{PhCF}_3$. However, this reaction does not work in the case of nitrobenzene due to its lack of reactivity.

Direct oxidation of iodoarenes to $\text{ArI}(\text{OCOCF}_3)_2$ is considered as a convenient method. The oxidation of iodoarenes by concd HNO_3 and $(\text{F}_3\text{CCO})_2\text{O}$ appears only for deactivated substrates.³ However, this procedure is accompanied with a vigorous evolution of toxic nitrogen oxides. In the sodium percarbonate method,⁷ it is not suitable for the preparation of $\text{NO}_2\text{C}_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$ isomers, and $m\text{-F}_3\text{CC}_6\text{H}_4\text{I}(\text{OCOCF}_3)_2$ is obtained in only 40% yield.

The oxidation of iodoarenes with trifluoroperoxyacetic acid seems to be the most suitable method,⁸ but preparation of trifluoroperoxyacetic acid requires 80% H₂O₂, which is not available commercially. Herein, an alternative, easy method for preparation of [bis(trifluoroacetoxy)iodo]arenes from iodoarenes have been reported.

b. Results and Discussion

The direct preparation of ArI(OCOCF₃)₂ has described from the respective iodoarenes in CF₃CO₂H, using commercial potassium peroxodisulfate, K₂S₂O₈, as the oxidant. For example, the reaction of iodobenzene in a mixed solvent of CF₃CO₂H and CH₂Cl₂ in the presence of K₂S₂O₈ at 36-38 °C for 20 h gave [bis(trifluoroacetoxy)iodo]benzene in 76% yield. The results are given in Table 3.1. The oxidation of iodoarenes to [bis(trifluoroacetoxy)iodo]arenes can be easily scaled up, and given the advantages of K₂S₂O₈ outlined above, together with the complete absence of effluent or byproduct problems. The direct method is described in Scheme 3.1.



Scheme 3.1

Table 3.1 Preparation of [Bis(trifluoroacetoxy)iodo]arenes from Iodoarenes^a

Entry	Iodoarenes	Yield (%)
1	C ₆ H ₅ I	76
2	4-ClC ₆ H ₄ I	87
3	3-CF ₃ C ₆ H ₄ I	82
4	3-NO ₂ C ₆ H ₄ I ^b	72
5	4-NO ₂ C ₆ H ₄ I ^b	71
6	4-FC ₆ H ₄ I	71
7	4-BrC ₆ H ₄ I	75
8	3,5-(CF ₃) ₂ C ₆ H ₃ I	36
9	4-ClC ₆ H ₄ I ^c	81
10	4-ClC ₆ H ₄ I ^{c,d}	79

^aThe reaction of an iodoarene (1 mmol) was carried out at 20 h at 36-38 °C in the presence of K₂S₂O₈ (4 mmol) in CF₃CO₂H (9 mL) and CH₂Cl₂ (2 mL).

^bCH₂Cl₂ (5 mL) was added.

^c1-Chloro-4-iodobenzene (5 mmol), K₂S₂O₈ (20 mmol), CF₃CO₂H (45 mL), and CH₂Cl₂ (10 mL) were added.

^dCF₃CO₂H (30 mL) was used.

The oxidative reactions shown in Scheme 3.1 was carried out at 36-38 °C in CF₃CO₂H. CH₂Cl₂ was added for dissolving iodoarenes completely. The presence of K₂S₂O₈ (in stoichiometric quantities) in the reaction mixture was indispensable, because without its addition the oxidation reactions did not proceed. Iodoarenes bearing strong-withdrawing

groups at the meta and para positions gave $\text{ArI}(\text{OCOCF}_3)_2$ in good yields, but the reaction of 1,3-bis(trifluoromethyl)-5-iodobenzene resulted in a low yield (36%) due to its lower reactivity. This method was not applicable for iodoarenes with strong electron-donating groups. For example, 4-iodotoluene and iodoanisoles were quickly oxidized in the reaction mixtures, but the reaction resulted in the decomposition to tarry products.

c. Experimental Section

Preparation of [Bis(trifluoroacetoxy)iodo]arenes from Iodoarenes

A solution of an appropriate iodoarenes (1 mmol) in a mixture of $\text{CF}_3\text{CO}_2\text{H}$ (9 mL) and CH_2Cl_2 (2 mL) was heated with stirring to 36-38 °C. Next, $\text{K}_2\text{S}_2\text{O}_8$ (4 mmol) was added portionwise during 10 min and the stirring was continued until TLC analysis indicated completion of the reaction. Reaction times needed 20 h. After completion of the reaction, water (10 mL) was added. The precipitated product was collected by filtration under reduced pressure, washed with CH_2Cl_2 (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with dichloromethane (3×10 mL), followed by drying (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation under reduced pressure. The crude product was washed with hexane (10 mL) and purified by recrystallization from $\text{CF}_3\text{CO}_2\text{H}$ /hexane.

Large scale synthesis was conducted for 1-[bis(trifluoroacetoxy)iodo]-4-chlorobenzene in a similar manner. A solution of 1-chloro-4-iodobenzene (1.196 g, 5 mmol) in a mixture of $\text{CF}_3\text{CO}_2\text{H}$ (45 mL) and CH_2Cl_2 (10 mL) was heated with stirring to 36-38 °C. Next, $\text{K}_2\text{S}_2\text{O}_8$ (20 mmol) was added portionwise over 20 min and the stirring was continued for 20 h. Workup of the reaction mixture gave the purified product (1.881 g, 81%). When $\text{CF}_3\text{CO}_2\text{H}$

was decreased from 45 to 30 mL under the above conditions, the yield was slightly decreased (1.841 g, 79%).

[Bis(trifluoroacetoxy)iodo]benzene

Yield: 0.335 g (76%); mp 119-120 °C (lit.² mp 120-121 °C).

¹H NMR (300 MHz, CDCl₃) δ = 7.62 (t, J = 8 Hz, 1 H, ArH), 7.74 (t, J = 8 Hz, 2 H, ArH), 8.20 (d, J = 8.0 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 161.07 (q, J_{CF} = 41 Hz, COCF₃), 135.14, 133.67, 132.02, 122.76, 112.84 (q, J_{CF} = 286 Hz, COCF₃).

1-[Bis(trifluoroacetoxy)iodo]-4-chlorobenzene

Yield: 0.404 g (87%); mp 129-130 °C (lit.^{6b} mp 131-133 °C).

¹H NMR (300 MHz, CDCl₃) δ = 7.58 (d, J = 9 Hz, 2 H, ArH), 8.14 (d, J = 9 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 161.15 (q, J_{CF} = 41 Hz, COCF₃), 140.84, 136.56, 132.38, 119.59, 112.82 (q, J_{CF} = 286 Hz, COCF₃).

1-[Bis(trifluoroacetoxy)iodo]-3-(trifluoromethyl)benzene

Yield: 0.416 g (82%); mp 96-97 °C (lit.² mp 99-100 °C).

¹H NMR (300 MHz, CDCl₃) δ = 7.80 (t, J = 8 Hz, 1 H, ArH), 8.0 (d, J = 8 Hz, 1 H, ArH), 8.39 (d, J = 8 Hz, 1 H, ArH), 8.44 (s, 1 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 161.23 (q, J_{CF} = 41 Hz, COCF₃), 138.12, 134.22 (q, J_{CF} = 34 Hz, CCF₃), 132.51, 131.82 (q, J_{CF} = 4 Hz, CCF₃), 130.42 (q, J_{CF} = 4 Hz, CCF₃), 122.30 (q, J_{CF} = 271 Hz, CCF₃), 121.79, 112.84 (q, J_{CF} = 286 Hz, COCF₃).

1-[Bis(trifluoroacetoxy)iodo]-3-nitrobenzene

Yield: 0.347 g (72%); mp 143-144 °C (lit.³ mp 143 °C).

¹H NMR (300 MHz, CDCl₃) δ = 7.87 (t, J = 8 Hz, 1 H, ArH), 8.51 (d, J = 8 Hz, 1 H, ArH), 8.55

(d, $J=8$ Hz, 1 H, ArH), 9.04 (s, 1 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 162.17 (q, J_{CF} = 43 Hz, COCF_3), 149.29, 141.02, 133.27, 130.77, 128.79, 121.42, 114.54 (q, J_{CF} = 282 Hz, COCF_3).

1-[Bis(trifluoroacetoxy)iodo]-4-nitrobenzene

Yield: 0.341 g (71%); mp 158-159 °C (lit.³ mp 161 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.41-8.49 (m, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 161.03 (q, J_{CF} = 44 Hz, COCF_3), 150.39, 136.31, 126.95, 126.83, 114.22 (q, J_{CF} = 284 Hz, COCF_3).

1-[Bis(trifluoroacetoxy)iodo]-4-fluorobenzene

Yield: 0.319 g (71%); mp 94-96 °C (lit.⁷ mp 103-105 °C).

^1H NMR (300 MHz, CDCl_3) δ = 7.29 (dd, J = 8.9 Hz, 2 H, ArH), 8.24 (dd, J = 5.9 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 165.31 (q, J_{CF} = 259 Hz, CF), 161.17 (q, J_{CF} = 41 Hz, COCF_3), 138.25 (q, J_{CF} = 9 Hz, CCCC), 119.76 (q, J_{CF} = 23 Hz, CCF), 116.38, 112.83 (q, J_{CF} = 286 Hz, COCF_3).

1-[Bis(trifluoroacetoxy)iodo]-4-bromobenzene

Yield: 0.384 g (75%); mp 125-127 °C.

^1H NMR (300 MHz, CDCl_3) δ = 7.74 (d, J = 9 Hz, 2 H, ArH), 8.05 (d, J = 9 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 161.18 (q, J_{CF} = 41 Hz, COCF_3), 136.53, 135.29, 129.23, 120.45, 112.82 (q, J_{CF} = 286 Hz, COCF_3).

Anal. Found: C, 23.48; H, 0.77%. Calcd for $\text{C}_{10}\text{H}_4\text{BrF}_6\text{IO}_4$: C, 23.60; H, 0.79%.

1-[Bis(trifluoroacetoxy)iodo]-3,5-bis(trifluoromethyl)benzene

Yield: 0.205 g (36%); mp 121-123 °C (lit.⁸ mp 83 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.27 (s, 1 H, ArH), 8.75 (s, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 162.76 (q, J_{CF} = 38 Hz, COCF_3), 134.81 (q, J_{CF} = 4 Hz, CCCF_3), 134.49 (q, J_{CF} = 34 Hz, CCF_3), 126.54 (q, J_{CF} = 4 Hz, CCCF_3), 23.57 (q, J_{CF} = 271 Hz, CCF_3), 123.29, 115.55 (q, J_{CF} = 287 Hz, COCF_3).

d. References

1. Applications of [bis(trifluoroacetoxy)iodo]arenes in organic synthesis: a) Tamura, Y.; Yakura, T.; Tohma, H.; Kikuchi, K.; Kita, Y. *Synthesis* **1989**, 126. b) Kita, Y.; Tohma, H.; Hatanaka, K.; Takada, T.; Fujita, S.; Mitoh, S.; Sakurai, H.; Oka, S. *J. Am. Chem. Soc.* **1994**, *116*, 3684. c) Takada, T.; Arisawa, M.; Gyoten, M.; Hamada, R.; Tohma, H.; Kita, Y. *J. Org. Chem.* **1998**, *63*, 7698. d) Moriarty, R. M.; Berglund, B. A.; Penmasta, R. *Tetrahedron Lett.* **1992**, *33*, 6065. e) Tamura, Y.; Yakura, T.; Shirouchi, Y.; Haruta, J. I. *Chem. Pharm. Bull.* **1986**, *34*, 1061. f) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 287. g) Benhida, R.; Blanchard, P.; Fourrey, J. L. *Tetrahedron Lett.* **1998**, *39*, 6849. h) Ley, S. V.; Schucht, O.; Thomas, A. W.; Murray, P. J. *J. Chem. Soc. Perkin Trans* **1999**, *10*, 1251. i) Kita, Y.; Yakura, T.; Terashi, H.; Haruta, J.; Tamura, Y. *Chem. Pharm. Bull.* **1989**, *37*, 891. j) Kanematsu, K.; Morita, S.; Fukushima, S.; Osawa, E. *J. Am. Chem. Soc.* **1981**, *103*, 5211. k) Kita, Y.; Thoma, H.; Inagaki, M.; Hatanaka, K. *Heterocycles* **1992**, *33*, 503. l) Gates, B. D.; Dalidowicz, P.; Tebben, A.; Wang, A.; Swenton, J. S. *J. Org. Chem.* **1992**, *57*, 2135. m) Loudon, G. M.; Radhakrishna, A. S.; Almond, M. R.; Blodgett, J. K.; Boutin, R. H. *J. Org. Chem.* **1984**, *49*, 4272. n) Kikugawa, Y.; Kawase, M. *Chem. Lett.* **1990**, *4*, 581. o) Kita, Y.; Takada, T.; Mihara, S.; Tohma, H. *Synlett* **1995**, *2*, 211. p) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. *Synthesis* **1980**, *6*, 486. q) Spyroudis, S.; Varvoglis, A. *J. Chem. Soc. Chem. Commun.* **1979**, *14*, 615. r) Sing, O. V. *Org. Prep. Proced. Int.* **1993**, *25*, 693.

2. Maletina, I. I.; Orda, V. V.; Yagupolskii, L. M. *Zh. Org. Khim.* **1974**, *10*, 294.
3. Yagupolskii, L. M.; Maletina, I. I.; Kondratenko, N. V.; Orda, V. V. *Synthesis* **1977**, 574.
4. Kasumov, T. M.; Brel, V. K.; Grishin, Y. K.; Zefirov, N. S.; Stang, P. J. *Tetrahedron* **1997**, *53*, 1145.
5. Zefirov, N. S.; Safronov, S. O.; Kaznacheev, A. A.; Zhdankin, V. V. *Zh. Org. Khim.* **1989**, *25*, 1807.
6. a) Spyroudis, S.; Varvoglis, A. *Synthesis* **1975**, *7*, 445. b) White, J. D.; Caravatti, G.; Kline, T. B.; Edstrom, E.; Rice, K. C.; Brossi, A. *Tetrahedron* **1983**, *39*, 2393.
7. Kazmierczak, P.; Skulski, L. *Molecules* **2002**, *7*, 810.
8. Zhdankin, V. V.; Scheuller, M. C.; Stang, P. J. *Tetrahedron Lett.* **1993**, *34*, 6853.

Chapter IV

Preparation of Diaryliodonium Salts

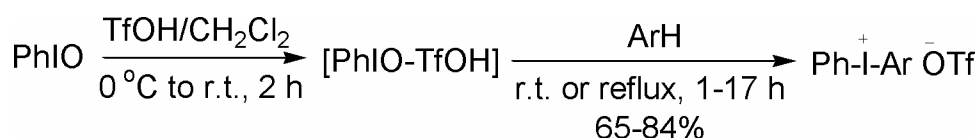
A. Direct Preparation of Diaryliodonium Triflates from Iodoarenes

a. Introduction

Diaryliodonium salts represent an important class of aromatic iodine(III) derivatives. They are used in organic synthesis mostly as arylating reagents for a large variety of organic and inorganic nucleophiles,¹ and have been applied to the photochemical polymerization process² and to chemical amplification in imaging systems.³ In addition, some of diaryliodonium salts have also shown biological activity.⁴ Diaryliodonium salts are generally solid compounds, mostly stable towards heat, oxygen, and humidity; they are mildly light-sensitive and should be stored in the dark, without refrigeration. Many methods have been described for the preparation of diaryliodonium salts,⁵ but very few of these involve the syntheses of diaryliodonium triflate and tosylate salts.

The methods used so far are generally as follows.

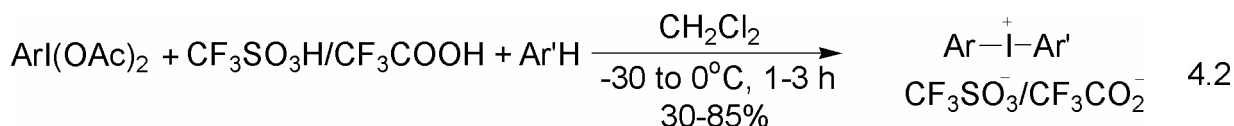
One-pot preparation of diaryliodonium triflates was described through the in situ preparation of a reactive hypervalent iodine(III) reagent from iodosylbenzene and triflic acid followed by its reaction with aromatic substrates.⁶



4.1

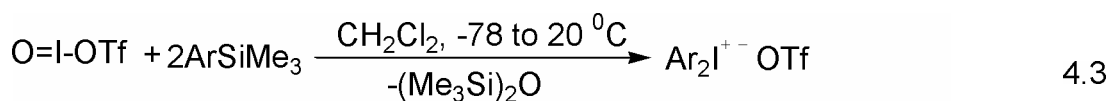
Ar = Ph, 4-MeC₆H₄, 2,5-Me₂C₆H₃, 2,4,6-Me₃C₆H₂,
4-MeOC₆H₄, 4-EtOC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄, 4-IC₆H₄

A convenient synthesis of diaryliodonium triflates was presented via the reaction of aromatic substrates with (diacetoxyiodo)arenes activated by triflic acid or trifluoroacetic acid.^{7,8}



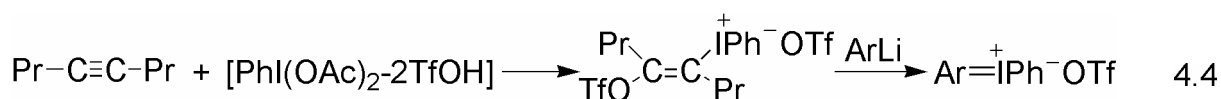
Ar = Ph, 2-MeC₆H₄, 3-MeC₆H₄, 2,4,6-Me₃C₆H₂, 3,5-Me₂C₆H₃, 3-MeOC₆H₄
 Ar' = 4-Bu^tC₆H₄, 4-MeC₆H₄, 4-MeOC₆H₄, 2,4,6-Me₃C₆H₂, 4-CMe₃CH₂C₆H₄

Diaryliodonium triflates were prepared by the reaction of iodosyl triflate with the trimethylsilyl derivatives of aromatic compounds.⁹



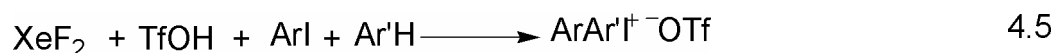
Ar = Ph, 4-MeC₆H₄, 2,4,6-Me₃C₆H₂, 4-BrC₆H₄, 4-(4'-BrC₆H₄)C₆H₄

Unsymmetrical diaryliodonium triflates were afforded by the treatment of β -(triflyloxy)vinyliodonium triflates with aryl lithium reagents.¹⁰



ArLi = 2-lithiobenzothiophene, 2-lithiothiophene, 2-lithiotoluene, 2-lithioanisole, 3-lithioanisole

Diaryliodonium triflates were produced by the reaction of xenon difluoride, triflic acid, iodoarenes and aromatic compounds.¹¹



Activated aromatic compounds reacted completely with the reagent [PhIO/TfOH] within an

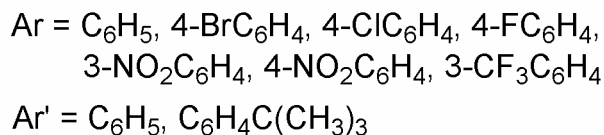
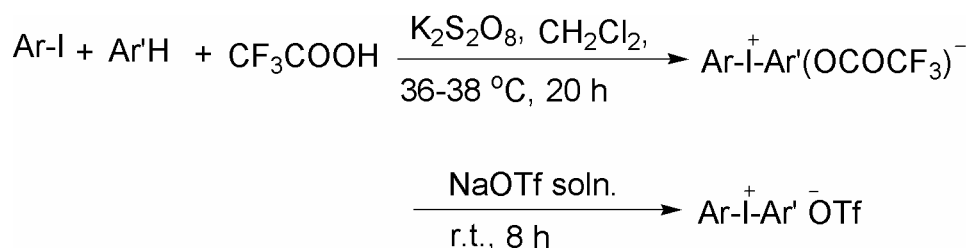
hour. Weakly deactivated aromatics needed prolonged reaction time to produce reasonable yields of the diaryliodonium triflates.⁶ Strongly deactivated aromatics such as nitrobenzene and benzonitrile did not give the corresponding diaryliodonium triflates. However, the reagent [PhIO/TfOH] also gives (*para*-phenylene)bis(aryliodonium)ditriflates as byproducts. Interaction of most aromatic substrates with [PhI(OAc)₂/2TfOH] employed in the present work gave high yields in the 0.5-1 h reaction at room temperature.⁷ It is noteworthy that halogenated benzenes require prolonged reaction time (24 h). However, this reagent also was not effective for strongly deactivated aromatics such as nitrobenzene and benzonitrile. The generality of the O=IOTf/ArSiMe₃/CH₂Cl₂ procedure is indicated by the preparation of various aromatic iodonium triflate salts bearing methyl, halogen and other substituents in the aromatic ring.⁹ However, the reaction has limited applicability in case of easily oxidizable aromatic substrates such as hydroxy, methoxy and amino derivatives. The reaction of β -(triflyloxy)vinyliodonium triflates with aryl lithium reagents affords unsymmetrical diaryliodonium triflates in good yields, which include synthetically difficult *ortho*- and *meta*-substituted aryliodonium triflates.¹⁰ Reaction of 2 equiv of triflic acid or trifluoroacetic acid with bis(acetoxy)iodoarenes gave an intermediate complex, [ArI(OAc)₂/CF₃SO₃H] or [ArI(OAc)₂/CF₃CO₂H]. These activated complexes were not isolated but were treated in situ with substituted benzene at low temperature (-30 to 0 °C).⁸

Considering the useful properties of salts and other derivatives of triflic acid,¹² the development of a simple and efficient procedure for the preparation of diaryliodonium triflates is a desirable goal. Easy preparation of [bis(trifluoroacetoxy)iodo]arenes [ArI(OCOCF₃)₂] from the respective iodoarenes in CF₃CO₂H, using K₂S₂O₈, as the oxidant at 36-38 °C for 20 h have reported in chapter III.¹³ ArI(OCOCF₃)₂ is a relatively reactive reagent

and can undergo arylation to give diaryliodonium salts. Therefore, it was expected that the reaction of iodoarenes with $K_2S_2O_8/CF_3CO_2H$ in the presence of appropriate arenes would give diaryliodonium salts. Herein a direct and effective method for the preparation of diaryliodonium triflates from iodoarenes is reported, which can be used as a strong acid generator.¹⁴

b. Results and Discussion

A simple, easy, efficient method for the direct preparation of diaryliodonium triflates, $Ar_2I^+OTf^-$ from iodoarenes was examined. At first, diaryliodonium trifluoroacetoxylates $[Ar_2I(OCOCF_3)]$ were prepared by the reaction of iodoarenes, CF_3CO_2H , and $K_2S_2O_8$ as the oxidant with aromatic substrates at 36-38 °C. CH_2Cl_2 was added for dissolving iodoarenes completely. Next, interaction of $Ar_2I^+(OCOCF_3)^-$ with sodium triflate (NaOTf) solution provided the corresponding diaryliodonium triflates at room temperature in fairly good yields. The results are given in Table 4.1.



Scheme 4.1

Table 4.1 Preparation of Diaryliodonium Triflates from Iodoarenes^a

Entry	Iodoarene (mmol)	Arenes (mmol)	Yield (%)
1	PhI	PhH	78
2	4-BrC ₆ H ₄ I	PhH	72
3	4-ClC ₆ H ₄ I	PhH	71
4	4-FC ₆ H ₄ I	PhH	73
5	4-NO ₂ C ₆ H ₄ I ^b	PhH	67
6	3-CF ₃ C ₆ H ₄ I	PhH	70
7	PhI	^t BuPh	69
8	4-BrC ₆ H ₄ I	^t BuPh	72
9	4-ClC ₆ H ₄ I	^t BuPh	68
10	4-FC ₆ H ₄ I	^t BuPh	72
11	4-NO ₂ C ₆ H ₄ I	^t BuPh	70
12	3-NO ₂ C ₆ H ₄ I	^t BuPh	58
13	3-CF ₃ C ₆ H ₄ I	^t BuPh	67

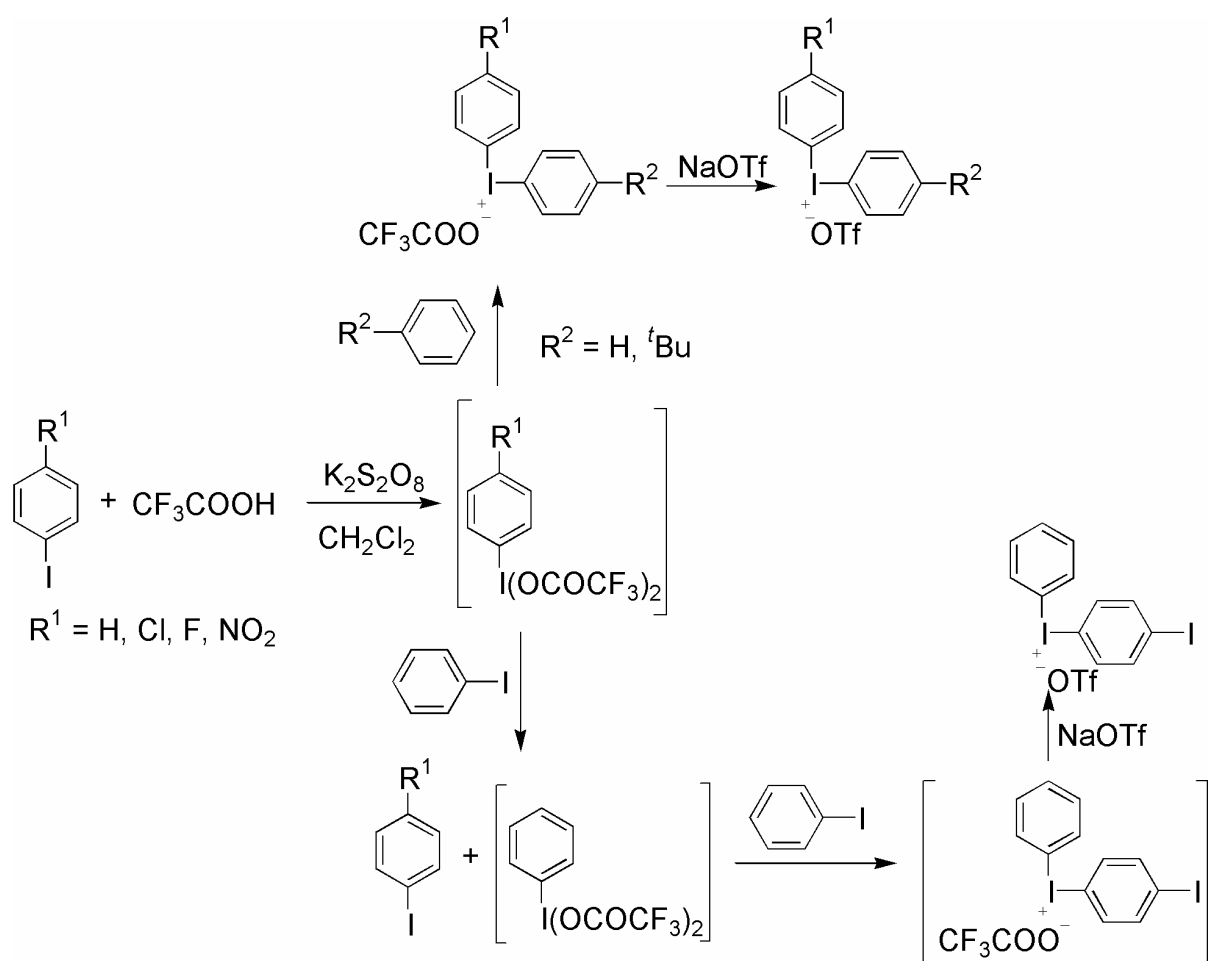
^aThe reaction of an iodoarene (1 mmol) was carried out in ArH (3 mmol), CF₃CO₂H (9 mL), and CH₂Cl₂ (2 mL) in the presence of K₂S₂O₈ (4 mmol) at 36-38 °C for 20 h. After workup, NaOTf solution was treated at room temperature for 8 h.

^bBenzene (3 mmol) was added after 20 h reaction and continued for another 8 h.

Deactivated aromatic iodides employed in the present work gave good yields together with the complete absence of effluent or byproduct problems. The novel method is described in Scheme 4.1. However, weakly deactivated aromatic substrates such as chlorobenzene and bromobenzene and an activated aromatic compound such as toluene resulted in low yields

(20-25%) due to their lower reactivity. This method was not applicable for iodoarenes with strong electron-donating groups and aromatic substrates with strong electron-donating groups. For example, iodoanisoles, iodonaphthalene, anisoles, naphthalene, etc., were quickly oxidized in the reaction mixtures, but the reaction resulted in decomposition and the formation of tarry products.

In the reaction of iodoarenes with aromatic substrates, the aromatic substrate was replaced by iodobenzene. Surprisingly, the reaction of 1-chloro-4-iodobenzene, 1-fluoro-4-iodobenzene, and 1-iodo-4-nitrobenzene gave (4-iodophenyl)(phenyl)iodonium triflate, the same product as from the reaction of iodobenzene. The formation of [bis(trifluoroacetoxy)iodo]arenes in the reaction of iodoarenes with $K_2S_2O_8$ /TFA, was described in chapter III. It is considered that [bis(trifluoroacetoxy)iodo]arenes were formed in situ and then underwent ligand transfer reactions with iodobenzene to form [bis(trifluoroacetoxy)iodo]benzene. This [bis(trifluoroacetoxy)iodo]benzene reacted with excess iodobenzene to give (4-iodophenyl)(phenyl)iodonium trifluoroacetate, which was treated with NaOTf solution to yield (4-iodophenyl)(phenyl)iodonium triflate (Scheme 4.2). Preliminarily, the reaction of 1-[bis(trifluoroacetoxy)iodo]-4-chlorobenzene with iodobenzene in TFA was conducted in order to confirm the ligand transfer reaction. The formation of [bis(trifluoroacetoxy)iodo]benzene in the reaction at 36-38 °C for 12 h was observed. Similar-type ligand transfer reactions were described in the reaction of hydroxy(tosyloxyiodo)benzene with iodoarenes.¹⁵ The results are given in Table 4.2.



Scheme 4.2

Table 4.2 Formation of (4-Iodophenyl)(phenyl)iodonium Triflate from Iodoarenes

Entry	Iodoarene (mmol)	Time (h)	Yield (%)
1	PhI	28	80
2	4-ClC ₆ H ₄ I	20	71
3	4-FC ₆ H ₄ I	20	73
4	4-NO ₂ C ₆ H ₄ I	28	68

^aThe reaction of an iodoarene (1 mmol) was carried out in CF₃CO₂H (9 mL), and CH₂Cl₂ (2 mL) in the presence of K₂S₂O₈ (4 mmol) at 36-38 °C for 20 h. PhI (3 mmol) was added after 20 h and the reaction was continued for another 8 h. After workup, NaOTf solution was treated at room temperature for 8 h.

c. Experimental Section

Optimized Procedure for Preparing Diaryliodonium Triflates from Iodoarenes

A solution of an appropriate iodoarene (1 mmol) in a mixture of an arene (3 mmol), CF₃CO₂H (9 mL) and CH₂Cl₂ (2 mL) was heated with stirring to 36-38 °C. Next, K₂S₂O₈ (4 mmol) was added portionwise during 10 min and the stirring was continued until TLC analysis indicated completion of reaction. Reaction time needed 20 h. After completion of the reaction, water (10 mL) was added. The precipitates were collected by filtration under reduced pressure, washed with CH₂Cl₂ (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with dichloromethane (3×10 mL) followed by drying (anhydrous Na₂SO₄), filtration, and removal of the solvent by evaporation under reduced pressure. The crude product was treated with NaOTf (10 mL) solution at room temperature for 8 h. The NaOTf solution was prepared by mixing with NaHCO₃ (1.0 g), H₂O (10 mL) and TfOH (1.5 mL). The precipitates were collected by filtration under reduced pressure, washed

with H₂O (10 mL), and dried in vacuo. Another crop was obtained by extraction of the filtrate with dichloromethane (3×10 mL) followed by drying (anhydrous Na₂SO₄), filtration, and removal of the solvent by evaporation under reduced pressure. The combined crude product was washed with hexane (10 mL), Et₂O (10 mL), and dried in vacuo. Further purification was conducted by repeating crystallization from CH₂Cl₂/hexane.

Diphenyliodonium triflate

Yield: 0.336 g (78%); mp 176-177 °C (lit.¹⁴ mp 178-180 °C).

¹H NMR (300 MHz, CD₃OD) δ = 8.17 (d, J = 8 Hz, 4 H, ArH), 7.69 (t, J = 8 Hz, 2 H, ArH), 7.50 (t, J = 8 Hz, 4 H, ArH).

¹³C NMR (75 MHz, CD₃OD) δ = 136.42, 133.62, 133.15, 121.80 (q, J_{CF} = 317.7 Hz, SO₂CF₃), 115.89.

(4-Bromophenyl)(phenyl)iodonium triflate

Yield: 0.365 g (72%); mp 131-132 °C (lit.⁷ mp 129-136 °C).

¹H NMR (300 MHz, CD₃OD) δ = 8.20 (d, J = 8 Hz, 2 H, ArH), 8.09 (d, J = 8 Hz, 2 H, ArH), 7.65-7.71 (m, 3 H, ArH), 7.53 (t, J = 8 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CD₃OD) δ = 138.08, 136.48, 136.19, 133.76, 133.21, 128.53, 121.77 (q, J_{CF} = 317.7 Hz, SO₂CF₃), 116.17, 114.13.

(4-Chlorophenyl)(phenyl)iodonium triflate

Yield: 0.331 g (71%); mp 108-110 °C (lit.⁶ mp 110-111 °C).

¹H NMR (300 MHz, CDCl₃) δ = 8.03 (d, J = 8 Hz, 2 H, ArH), 7.98 (d, J = 8 Hz, 2 H, ArH), 7.50 (t, J = 8 Hz 1 H, ArH), 7.40 (t, J = 8 Hz, 2 H, ArH), 7.34 (d, J = 8 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CDCl₃) δ = 139.27, 136.73, 135.38, 132.43, 132.13, 132.07, 120.04 (q, J_{CF} = 317.7 Hz, SO₂CF₃), 114.12, 110.86.

(4-Fluorophenyl)(phenyl)iodonium triflate¹⁶

Yield: 0.329 g (73%); mp 133-134 °C.

¹H NMR (300 MHz, CD₃OD) δ = 8.25-8.16 (m, 4 H, ArH), 7.69 (t, J = 8 Hz, 1 H, ArH), 7.53 (t, J = 8 Hz, 2 H, ArH), 7.29 (t, J = 8 Hz, 2 H, ArH).

¹³C NMR (75MHz, CD₃OD) δ = 166.42 (d, J_{CF} = 252.2 Hz, CF), 139.32 (d, J_{CF} = 8.7 Hz, CCCC), 136.36, 133.73, 133.21, 121.80 (q, J_{CF} = 315.8 Hz, SO₂CF₃), 120.54 (d, J_{CF} = 23.5 Hz, CCF), 116.39, 109.76.

(4-Nitrophenyl)(phenyl)iodonium triflate

Yield: 0.316 g (67%); mp 189-190 °C.

¹H NMR (300 MHz, CD₃OD) δ = 8.43 (d, J = 9 Hz, 2 H, ArH), 8.30 (d, J = 9 Hz, 2 H, ArH), 8.27 (d, J = 8 Hz, 2 H, ArH), 7.73 (t, J = 8 Hz, 1 H, ArH), 7.57 (t, J = 8 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CD₃OD) δ = 151.47, 137.67, 136.86, 134.07, 133.42, 127.45, 121.77 (q, J_{CF} = 316.5 Hz, SO₂CF₃), 121.56, 116.18.

Anal. Found: C, 32.91; H, 1.90; N, 2.98%. Calcd for C₁₃H₉O₅NIF₃S: C, 32.85; H, 1.89; N, 2.95%.

(3-Trifluoromethylphenyl)(phenyl)iodonium triflate

Yield: 0.351 g (70%); mp 107-108 °C.

¹H NMR (300 MHz, CD₃OD) δ = 8.59 (s, 1 H, ArH), 8.45 (d, J = 8 Hz, 1 H, ArH), 8.25 (d, J = 8 Hz, 2 H, ArH), 7.99 (d, J = 8 Hz, 1 H, ArH), 7.72 (t, J = 8 Hz, 2 H, ArH), 7.56 (t, J = 8 Hz, 2 H, ArH).

¹³C NMR (75 MHz, CD₃OD) δ = 140.10, 136.68, 134.46 (q, J_{CF} = 33.4 Hz, CCF₃), 133.94, 133.80, 133.30, 133.08 (q, J_{CF} = 3.7 Hz, CCCC), 130.29 (q, J_{CF} = 3.7 Hz, CCCC), 124.13 (q, J_{CF} = 270.2 Hz, CCF₃), 121.77 (q, J_{CF} = 316.5 Hz, SO₂CF₃), 116.31, 116.05.

Anal. Found: C, 33.77; H, 1.77%. Calcd for C₁₄H₉O₃IF₆S: C, 33.74; H, 1.81%.

(4-*tert*-Butylphenyl)(phenyl)iodonium triflate

Yield: 0.344 g (69%); mp 162-163 °C (lit.⁷ mp 163-165 °C).

¹H NMR (300 MHz, CD₃OD) δ = 8.17 (d, *J* = 8 Hz, 2 H, ArH), 8.09 (d, *J* = 8 Hz, 2 H, ArH), 7.66 (t, *J* = 7 Hz, 1 H, ArH), 7.58-7.49 (m, 4 H, ArH), 1.30 (s, 9H, Me).

¹³C NMR (75 MHz, CD₃OD) δ = 157.77, 136.34, 136.25, 133.53, 133.09, 130.48, 121.75 (q, *J*_{CF} = 315.9 Hz, SO₂CF₃), 115.97, 112.39, 36.08, 31.30.

(4-Bromophenyl)(4-*tert*-butylphenyl)iodonium triflate

Yield: 0.416 g (72%); mp 199-200 °C.

¹H NMR (300 MHz, CD₃OD) δ = 8.11 (d, *J* = 9 Hz, 2 H, ArH), 8.07 (d, *J* = 8.7 Hz, 2 H, ArH), 7.65 (d, *J* = 9 Hz, 2 H, ArH), 7.58 (d, *J* = 9.0 Hz, 2 H, ArH), 1.31 (s, 9H, Me).

¹³C NMR (75MHz, CD₃OD) δ = 157.97, 137.99, 136.30, 136.15, 130.57, 128.45, 121.78 (q, *J*_{CF} = 316.5 Hz, SO₂CF₃), 114.18, 112.64, 36.10, 31.30.

Anal. Found: C, 36.15; H, 3.02%. Calcd for C₁₇H₁₇O₃IBrF₃S: C, 36.12; H, 3.01%.

(4-*tert*-Butylphenyl)(4-chlorophenyl)iodonium triflate

Yield: 0.372 g (68%); mp 178-179 °C.

¹H NMR (300 MHz, CD₃OD) δ = 8.13 (d, *J* = 9 Hz, 2 H, ArH), 8.08 (d, *J* = 9 Hz, 2 H, ArH), 7.58 (d, *J* = 9.0 Hz, 2 H, ArH), 7.53 (d, *J* = 9 Hz, 2 H, ArH), 1.31 (s, 9H, Me).

¹³C NMR (75MHz, CDCl₃) δ = 157.89, 140.15, 137.96, 136.30, 133.11, 130.53, 121.76 (q, *J*_{CF} = 316.4 Hz, SO₂CF₃), 113.36, 112.69, 36.06, 31.29.

Anal. Found: C, 39.22; H, 3.26%. Calcd for C₁₇H₁₇O₃IClF₃S: C, 39.20; H, 3.27%.

(4-*tert*-Butylphenyl)(4-fluorophenyl)iodonium triflate

Yield: 0.371 g (72%); mp 137-138 °C.

^1H NMR (300 MHz, CD_3OD) δ = 8.23 (dd, J = 5 Hz, 2 H, ArH), 8.10 (d, J = 8 Hz, 2 H, ArH), 7.58 (d, J = 8 Hz, 2 H, ArH), 7.29 (d, J = 8 Hz, 2 H, ArH), 1.31 (s, 9H, Me).

^{13}C NMR (75MHz, CD_3OD) δ = 166.33 (d, J_{CF} = 252.2 Hz, CF), 157.90, 139.25 (d, J_{CF} = 9.3 Hz, CCCC), 136.18, 130.53, 121.79 (q, J_{CF} = 315.8 Hz, SO_2CF_3), 120.46 (d, J_{CF} = 22.9 Hz, CCF), 112.88, 109.81, 36.11, 31.31.

Anal. Found: C, 40.50; H, 3.34%. Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_3\text{IF}_4\text{S}$: C, 40.48; H, 3.37%.

(4-*tert*-Butylphenyl)(4-nitrophenyl)iodonium triflate

Yield: 0.375 g (70%); mp 151-152 °C.

^1H NMR (300 MHz, CD_3OD) δ = 8.42 (d, J = 9.0 Hz, 2 H, ArH), 8.30 (d, J = 9.0 Hz, 2 H, ArH), 8.17 (d, J = 9.0 Hz, 2 H, ArH), 7.61 (d, J = 9.0 Hz, 2 H, ArH), 1.31 (s, 9H, Me).

^{13}C NMR (75MHz, CD_3OD) δ = 158.32, 151.42, 137.56, 136.66, 130.76, 127.43, 121.76 (q, J_{CF} = 316.42 Hz, SO_2CF_3), 121.65, 112.65, 36.16, 31.29.

(4-*tert*-Butylphenyl)(3-nitrophenyl)iodonium triflate

Yield: 0.335 g (58%); mp 159-160 °C.

^1H NMR (300 MHz, CD_3OD) δ = 9.08 (t, J = 2 Hz, 1 H, ArH), 8.53 (d, J = 8 Hz, 1 H, ArH), 8.49 (dd, J = 8 Hz, 1 H, ArH), 8.18 (d, J = 8 Hz, 2 H, ArH), 7.78 (t, J = 8 Hz, 1 H, ArH), 7.61 (d, J = 8.0 Hz, 2 H, ArH), 1.31 (s, 9H, Me).

^{13}C NMR (75MHz, CD_3OD) δ = 158.37, 150.40, 141.83, 136.58, 133.95, 131.02, 130.76, 128.09, 121.78 (q, J_{CF} = 316.50 Hz, SO_2CF_3), 115.63, 112.86, 36.19, 31.30.

Anal. Found: C, 38.53; H, 3.26; N, 2.64%. Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_5\text{F}_3\text{NIS}$: C, 38.43; H, 3.20; N, 2.64%.

(4-*tert*-Butylphenyl)(3-trifluoromethylphenyl)iodonium triflate

Yield: 0.375 g (67%); mp 162-163 °C.

^1H NMR (300 MHz, CD_3OD) δ = 8.57 (s, 1 H, ArH), 8.42 (d, J = 8 Hz, 1 H, ArH), 8.15 (d, J = 8 Hz, 2 H, ArH), 7.99 (d, J = 8 Hz, 1 H, ArH), 7.73 (t, J = 8 Hz, 1 H, ArH), 7.60 (d, J = 8 Hz, 2 H, ArH), 1.32 (s, 9H, Me).

^{13}C NMR (75 MHz, CD_3OD) δ = 158.26, 139.99, 136.46, 134.47 (q, J_{CF} = 33.4 Hz, CCF_3), 133.81, 133.01 (q, J_{CF} = 4.4 Hz, CCCF_3), 130.69, 130.29 (q, J_{CF} = 3.1 Hz, CCCF_3), 124.19 (q, J_{CF} = 270.2 Hz, CCF_3), 121.79 (q, J_{CF} = 316.5 Hz, SO_2CF_3), 116.12, 112.77, 36.18, 31.30.

Anal. Found: C, 39.03; H, 3.07%. Calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3\text{IF}_6\text{S}$: C, 39.00; H, 3.07%.

(4-Iodophenyl)(phenyl)iodonium triflate

Yield: 0.476 g (80%); mp 138-140 °C (lit.⁶ mp 144-148 °C).

^1H NMR (300 MHz, CD_3OD) δ = 8.17 (d, J = 8 Hz, 2 H, ArH), 7.91-7.85 (m, 4 H, ArH), 7.69 (t, J = 8 Hz, 1 H, ArH), 7.53 (t, J = 8 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CD_3OD) δ = 142.23, 137.75, 136.45, 133.73, 133.20, 121.73 (q, J_{CF} = 316.4 Hz, SO_2CF_3), 116.04, 115.12, 100.59.

d. References

1. a) Chen, D.-J.; Chen, Z.-C. *Synlett* **2000**, 1175. b) Wang, L.; Chen, Z.-C. *Synth. Commun.* **2000**, *30*, 3607. c) Radhakrishnan, U.; Stang, P. J. *Org. Lett.* **2001**, *3*, 859. d) Crivello, J. V.; Bulut, U. *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *88*, 290. e) Zhang, B.-X.; Nuka, T.; Fujiwara, Y.; Yamaji, T.; Hou, Z.; Kitamura, T. *Heterocycles* **2004**, *64*, 199. f) Zhou, T.; Chen, Z.-C. *Synth. Commun.* **2002**, *32*, 887. g) Wang, L.; Chen, Z.-C. *J. Chem. Res. Synop.* **2000**, 372. h) Zhou, T.; Chen, Z.-C. *Synth. Commun.* **2002**, *32*, 903. i) Makioka, Y.; Fujiwara, Y.; Kitamura, T. *J. Organomet. Chem.* **2002**, *611*, 509. j) Wang, F.-Y.; Chen, Z.-C.; Zheng, Q.-G. *J. Chem. Res. Synop.* **2003**, 810. k) Davydov, D. V.; Beletskaya, I. P.; Leninsky, G. *Tetrahedron*

- Lett.* **2002**, 43, 6217. l) Kang, S.-K.; Yamaguchi, T.; Ho, P.-S.; Kim, W.-Y.; Ryu, H.-C. *J. Chem. Soc. Perkin Trans. 1* **1998**, 841. m) Hou, R.-S.; Wang, H.-M.; Lin, Y.-C.; Chen, L.-C. *J. Chin. Chem. Soc.* **2005**, 52, 1029. n) Zhou, T.; Chen, Z.-C. *Heteroatom. Chem.* **2002**, 13, 617. o) Wang, L.; Chen, Z.-C.; Zheng, Q.-G. *Chin. J. Chem.* **2002**, 20, 1457. p) Zhou, T.; Chen, Z.-C. *J. Chem. Res. Synop.* **2001**, 235.
2. a) Crivello, J. V. *Adv. Polym. Sci.* **1984**, 62, 1. b) Pappas, S. P. *Prog. Org. Coat.* **1985**, 13, 35. c) Yagci, Y.; Schnabel, W. *Makromol. Chem. Macromol. Symp.* **1988**, 13/14, 161. d) Wilson, C. G.; Bowden, M. J. *CHEMTECH* **1989**, 19, 182.
3. Ito, H.; Ueda, M. *J. Photopolym. Sci. Technol.* **1989**, 2, 1.
4. Koser, G. F. *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, **1983**; Chapter 25.
5. a) Zefirov, N. S.; Kasumov, T. M.; Koz'min, A. S.; Sorokin, V. D.; Stang, P. J.; Zhdankin, V. V. *Synthesis* **1993**, 1209. b) Beringer, F. M.; Dresler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* **1953**, 75, 2705. c) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, 81, 342. d) Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1972**, 37, 1516. e) Tyrra, W.; Butter, H.; Naumann, D. *J. Fluorine Chem.* **1993**, 60, 79. f) Beringer, F. M.; Dehn, J. W.; Winicov, M. *J. Am. Chem. Soc.* **1960**, 82, 2948. g) Schmeisser, M.; Dahmen, K.; Sartori, P. *Chem. Ber.* **1970**, 103, 307. h) Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Heterocycl. Chem.* **1992**, 29, 815. i) Beringer, F. M.; Lillien, I. *J. Am. Chem. Soc.* **1960**, 82, 725. j) Kasumov, T. M.; Brel, V. K.; Kozmin, A. S.; Zefirov, N. S. *Synthesis* **1995**, 775.
6. Kitamura, T.; Matsuyuki, J.; Nagata, K.; Furuki, R.; Taniguchi, H. *Synthesis* **1992**, 945.
7. Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *Synthesis* **1994**, 147.

8. Shah, A.; Pike, V. W.; Widdowson, D. A. *J. Chem. Soc. Perkin Trans. 1* **1997**, 2463.
9. Stang, P. J.; Zhdankin, V. V.; Tykwinski, R.; Zefirov, N. S. *Tetrahedron Lett.* **1991**, 32, 7497.
10. Kitamura, T.; Kotani, M.; Fujiwara, Y. *Tetrahedron Lett.* **1996**, 37, 3721.
11. Kasumov, T. M.; Brel, V. K.; Kozmin, A. S.; Zefirov, N. S.; Potekhin, K. A.; Stang, P. J. *New J. Chem.* **1997**, 21, 1347.
12. For reviews see: a) Huang, W.-Y.; Chen, Q.-Y. *The Chemistry of Sulfonic Acids, Esters and Their Derivatives*, Patai, S.; Rappoport, Z. Eds; Chichester, Wiley-Interscience, **1991**, Chapter 21, p. 903. b) Stang, P. J.; White, M. R. *Aldrichimica Acta* **1983**, 16, 15. c) Howells, R. D.; Mc Cown, J. D. *Chem. Rev.* **1977**, 77, 69. d) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.
13. Hossain, M. D.; Kitamura, T. *Bull. Chem. Soc. Jpn.* **2006**, 79, 142.
14. Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, 55, 639.
15. Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1980**, 45, 1542.
16. Shah, A.; Pike, V. W.; Widdowson, D. A. *J. Chem. Soc. Perkin Trans. 1* **1998**, 2043.

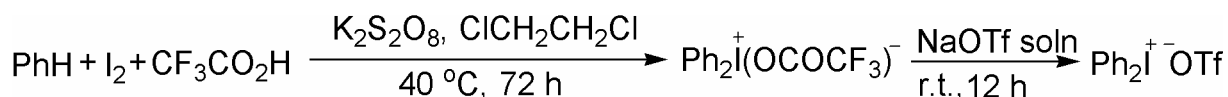
B. Direct and Simple Synthesis of Diaryliodonium Triflates from Arenes with Potassium Peroxodisulfate as the Oxidant

a. Introduction

The most ideal procedure for diphenyliodonium triflate should involve a straightforward synthesis from benzene and iodine. This procedure gives a direct and efficient method that does not contain the step via iodobenzene synthesis. However, probably, there are no methods for preparing diphenyliodonium triflate directly from benzene and iodine. In chapter III, it was reported that easy preparation of [bis(trifluoroacetoxy)iodo]arenes $[\text{ArI}(\text{OCOCF}_3)_2]$ from respective iodoarenes in TFA, using $\text{K}_2\text{S}_2\text{O}_8$, as the oxidant.¹ It was found (Chapter IV A) that diaryliodonium salts were formed by the reaction of some iodoarenes with aromatic substrates in the presence of $\text{K}_2\text{S}_2\text{O}_8$ in TFA.² During the course of systematic studies on effective and easy preparation of hypervalent iodine compounds, a simpler and more convenient method for preparing $\text{ArI}(\text{OCOCF}_3)_2$ was examined. This simple and convenient system consisted of arenes and molecular iodine. It is expected that diaryliodonium salts would be formed when iodoarenes were produced in situ in the reaction of arenes with iodine. Thus the reaction of arenes with molecular iodine in the presence of $\text{K}_2\text{S}_2\text{O}_8$ in TFA was conducted, followed by treatment with NaOTf. Herein, a direct, easy method for the preparation of diphenyliodonium triflate from benzene is described. Also, an application to *tert*-butylbenzene, toluene and less reactive halobenzenes is presented.

b. Results and Discussion

The direct method for the preparation of diphenyliodonium triflate [$\text{Ph}_2\text{I}(\text{OTf})$] from benzene and iodine was examined. At first, the reaction of benzene with elemental iodine was conducted in TFA in the presence of $\text{K}_2\text{S}_2\text{O}_8$ as the oxidant at 40 °C, where diphenyliodonium trifluoroacetate [$\text{Ph}_2\text{I}(\text{OCOCF}_3)$] was formed. 1,2-Dichloroethane was added for dissolving iodine completely. Next, $\text{Ph}_2\text{I}^+(\text{OCOCF}_3)^-$ was treated with aqueous NaOTf solution at room temperature to provide the corresponding diphenyliodonium triflate. The outline is shown in Scheme 4.3.



Scheme 4.3

Table 4.3 Optimization for Preparation of Diphenyliodonium Triflate^a

Entry	Benzene (mmol)	I ₂ (mmol)	K ₂ S ₂ O ₈ (mmol)	TFA (mL)	ClCH ₂ CH ₂ Cl (mL)	Time (h)	Yield (%)
1	4	0.5	4	9	5	48	48
2	10	0.5	4	9	5	72	58
3	10	0.5	5	9	5	72	66
4	10	0.5	6	9	5	72	64
5	20	0.5	5	9	5	72	45
6	10	0.5	5	10	5	72	71
7	100	5	50	100	50	72	69

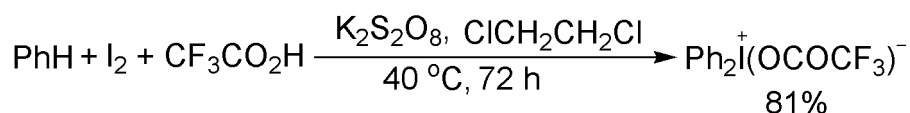
^aThe reaction of benzene with iodine was carried out in TFA and 1,2-dichloroethane in the presence of

$\text{K}_2\text{S}_2\text{O}_8$ at 40 °C. Then, the reaction mixture was treated with NaOTf solution at room temperature for 12 h.

Table 4.3 summarizes the results obtained by optimization of the preparation of diphenyliodonium triflate. The reaction of benzene (4 mmol) with iodine (0.5 mmol) was carried out in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (4 mmol) in TFA and 1,2-dichloroethane at 40 °C for 48 h. After treatment with aqueous NaOTf, diphenyliodonium triflate was obtained in 48% yield (entry 1). Use of 10 mmol of benzene gave diphenyliodonium triflate in 58% yield (entry 2). Use of 5 mmol of $\text{K}_2\text{S}_2\text{O}_8$ led to better yield, 66%, but further improvement was observed in the case of 6 mmol of $\text{K}_2\text{S}_2\text{O}_8$ (entries 3 and 4). Increase of benzene from 10 to 20 mmol decreased the yield, 45% (entry 5). The best result, 71% yield, was obtained by using benzene (10 mmol), iodine (0.5 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol), TFA (10 mL), and 1,2-dichloroethane (5 mL) (entry 6). The direct conversion of benzene to diphenyliodonium triflate can be easily scaled up and has the advantages of $\text{K}_2\text{S}_2\text{O}_8$ outlined above, together with the complete absence of effluent or byproduct problems. When the reaction of benzene (100 mmol) with iodine (5 mmol) was conducted in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (50 mmol) in TFA (100 mL) and 1,2-dichloroethane (50 mL) under the same conditions, diphenyliodonium triflate was obtained in 69% yield (entry 7). No large decrease of the yield was observed even in the case of the 10-fold scale experiment.

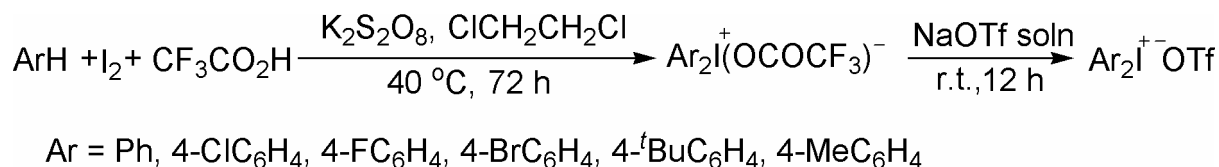
As described above, the reaction of benzene with iodine in the presence of $\text{K}_2\text{S}_2\text{O}_8$ initially affords diphenyliodonium trifluoroacetate, which is subject to exchange acetate with triflate to give diphenyliodonium triflate. To confirm the formation of diphenyliodonium trifluoroacetate, the isolation of diphenyliodonium trifluoroacetate was examined. The reaction mixture was worked up without the treatment with aqueous NaOTf solution. After completion of the reaction according to entry 6 in Table 4.3, the reaction mixture was

quenched with water and the product was extracted with CH₂Cl₂. Evaporation of the solvent gave diphenyliodonium trifluoroacetate in 81% yield, as shown in Scheme 4.4. This result indicates that diphenyliodonium trifluoroacetate is formed at the first step, and then it is converted to diphenyliodonium triflate by anion exchange.



Scheme 4.4

In order to explore the scope of this reaction, it is applied to other aromatic substrates. The outline is shown in Scheme 4.5. The results are given in Table 4.4. Arenes bearing weakly deactivated groups such as chloro, bromo, and fluoro groups gave diaryliodonium triflates in good yields. However, a similar reaction of iodobenzene did not give bis(4-iodophenyl)-iodonium triflate but afforded (4-iodophenyl)(phenyl)iodonium triflate in 69% yield. In the reaction of iodobenzene, it is considered that the iodo group of iodobenzene is oxidized to form [bis(trifluoroacetoxy)iodo]benzene, which reacts with iodobenzene to yield the (4-iodophenyl)(phenyl)iodonium salt. *tert*-Butylbenzene also gave bis(4-*tert*-butylphenyl)iodonium triflate in good yield, but toluene afforded bis(4-methylphenyl)iodonium triflate only in 11% yield. This method was not applicable for electron-rich arenes such as anisole, mesitylene, and *p*-xylene. For example, in the case of anisole, the reaction mixture was quickly oxidized to indicate black color, but no diaryliodonium salts were obtained. This method was not effective for arenes with strong electron-withdrawing groups such as trifluoromethyl and nitro groups due to their decreased reactivity.



Scheme 4.5

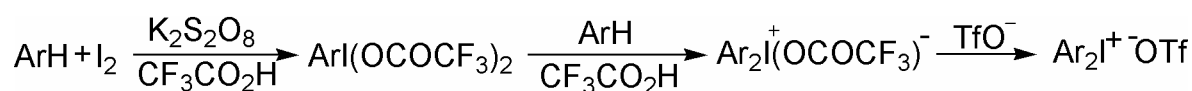
Table 4.4 Preparation of Diaryliodonium Triflates from Arenes^a

Entry	Arene	Product	Yield (%)
1	Chlorobenzene	(4-ClC ₆ H ₄) ₂ I ⁺ TfO ⁻	57
2	Bromobenzene	(4-BrC ₆ H ₄) ₂ I ⁺ TfO ⁻	54
3	Fluorobenzene	(4-FC ₆ H ₄) ₂ I ⁺ TfO ⁻	60
4	Iodobenzene	(4-IC ₆ H ₄) ₂ I ⁺ TfO ⁻	69
5	<i>tert</i> -Butylbenzene	(4- ^t BuC ₆ H ₄) ₂ I ⁺ TfO ⁻	55
6	Toluene	(4-MeC ₆ H ₄) ₂ I ⁺ TfO ⁻	11

^aThe reaction of an arene (10 mmol) was carried out in TFA (10 mL), 1,2-dichloroethane (5 mL) and iodine (0.5 mmol) in the presence of K₂S₂O₈ (5 mmol) at 40 °C for 72 h. Then, the reaction mixture was treated with NaOTf solution at room temperature for 12 h.

From the above results, it is considered that the reaction proceeds with three major fundamental steps: bis(trifluoroacetoxy)iodination, arylation, and anion exchange (scheme 4.6). The key step is the first bis(trifluoroacetoxy)iodination. The in situ formation of [bis(trifluoroacetoxy)iodo]arenes is a novel direct reaction from arenes and iodine promoted by K₂S₂O₈. Although a similar Selectfluor-promoted preparation of difluoriodoarenes or (diacetoxyiodo)arenes has been reported,³ there are no reports on the synthesis of

[bis(trifluoroacetoxy)iodo]arenes. According to the literature,^{3,4} the Selectfluor-promoted reaction seems to be applicable only for electron-rich aromatics. The mechanism on the formation of [bis(trifluoroacetoxy)iodo]arenes is not clear, but it is considered that the mechanism involves the oxidation of iodoarenes by K₂S₂O₈ because iodoarenes are efficiently oxidized by K₂S₂O₈ in TFA to give [bis(trifluoroacetoxy)iodo]arenes (Chapter III).¹ Once [bis(trifluoroacetoxy)iodo]arenes are formed, they immediately react with arenes to yield diaryliodonium trifluoroacetates.² Finally, exchange of anions in the diaryliodonium salts is well recognized and occurs easily.



Scheme 4.6

The present method described above covers relatively electron-rich to weakly deactivated aromatic substrates. This method involves fundamental starting materials (simple arenes and elemental iodine, and commercial K₂S₂O₈). The simple and convenient procedure for diaryliodonium triflates has a significant advantage over the previous reported ones (Chapter IV A).

c. Experimental Section

Optimized Procedure for Preparing Diaryliodonium Triflates from Arenes

A solution of the appropriate arene (10 mmol) in a mixture of molecular iodine (0.5 mmol), TFA (10 mL), and 1,2-dichloroethane (5 mL) was heated with stirring to 40 °C. After dissolving iodine, K₂S₂O₈ (5 mmol) was added. The reaction mixture was stirred at that temperature for 72 h. After completion of the reaction, water (20 mL) was added. The resulting precipitates were collected by filtration under reduced pressure, washed with CH₂Cl₂

(10 mL), and discarded. The crude product was obtained by extraction of the filtrate with CH_2Cl_2 (3×10 mL), followed by drying (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation. The crude product was treated with aqueous NaOTf (ca. 1 M, 10 mL) solution at room temperature for 12 h. The precipitates were collected by filtration under reduced pressure, washed with H_2O (10 mL), and dried in vacuo. Another crop was obtained by extraction of the filtrate with dichloromethane (3×10 mL), followed by drying (anhydrous Na_2SO_4), filtration, and removal of the solvent by evaporation. The combined crude product was recrystallized from CH_2Cl_2 /hexane.

Large-scale synthesis was conducted for diphenyliodonium triflate in a similar manner. A solution of benzene (7.9 g, 100 mmol) in a mixture of TFA (100 mL), 1,2-dichloroethane (50 mL), and I_2 (1.28 g, 5 mmol) was heated with stirring to 40 °C. After dissolving iodine, $\text{K}_2\text{S}_2\text{O}_8$ (50 mmol) was added, and the stirring was continued for 72 h, followed by treatment with NaOTf (ca. 1 M, 100 mL). Workup of the reaction mixture gave pure product (2.97 g, 69%).

Diphenyliodonium triflate

Yield: 0.316 g (71%); mp 177-178 °C (lit.⁵ mp 178-180 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.17 (d, J = 7.5 Hz, 4 H, ArH), 7.70 (t, J = 7.5 Hz, 2 H, ArH), 7.51 (t, J = 7.5 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 136.43, 133.65, 133.16, 121.81 (q, J_{CF} = 315.9 Hz, SO_2CF_3), 115.93.

Bis(4-chlorophenyl)iodonium triflate⁶

Yield: 0.294 g (57%); mp 175-176 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.05 (d, J = 8.1 Hz, 4 H, ArH), 7.58 (d, J = 8.1 Hz, 4 H,

ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 140.56, 138.07, 133.34, 121.77 (q, J_{CF} = 316.4 Hz, SO_2CF_3), 113.64.

Bis(4-bromophenyl)iodonium triflate

Yield: 0.326 g (54%); mp 190-191 °C (lit.⁷ mp 198 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.08 (d, J = 8.7 Hz, 4 H, ArH), 7.70 (d, J = 8.7 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 138.11, 136.34, 128.80, 121.80 (q, J_{CF} = 316.50 Hz, SO_2CF_3), 114.35.

Bis(4-fluorophenyl)iodonium triflate⁸

Yield: 0.292 g (60%); mp 167-168 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.25-8.21 (m, 4 H, ArH), 7.31 (t, J = 8.4 Hz, 4 H, ArH).

^{13}C NMR (75MHz, CDCl_3) δ = 166.43 (d, J_{CF} = 252.22 Hz, CF), 139.29 (d, J_{CF} = 8.6 Hz, CCF), 121.81 (q, J_{CF} = 316.5 Hz, SO_2CF_3), 120.57 (d, J_{CF} = 22.87 Hz, CCF), 110.19.

Bis(4-tert-butylphenyl)iodonium triflate⁹

Yield: 0.311 g (55.0%); mp 164-165 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.09 (d, J = 8.4 Hz, 4 H, ArH), 7.56 (d, J = 8.4 Hz, 4 H, ArH), 1.29 (s, 18 H, Me).

^{13}C NMR (75 MHz, CDCl_3) δ = 157.65, 136.13, 130.42, 121.75 (q, J_{CF} = 316.5 Hz, SO_2CF_3), 36.03, 31.32.

(4-Iodophenyl)(phenyl)iodonium triflate

Yield: 0.404 g (69%); mp 138-140 °C (lit.¹⁰ mp 144-148 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.19 (d, J = 8.4 Hz, 2 H, ArH), 7.92 (d, J = 8.4 Hz, 2 H,

ArH), 7.84 (d, $J = 8.4$ Hz, 2 H, ArH), 7.70 (t, $J = 8.4$ Hz, 1 H, ArH), 7.53 (t, $J = 8.4$ Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 142.24, 137.75, 136.46, 133.73, 133.20, 121.73$ (q, $J_{\text{CF}} = 316.5$ Hz, SO_2CF_3), 116.01, 115.10, 100.58.

Bis(4-methylphenyl)iodonium triflate

Yield: 0.054 g (11.2%); mp 182-184 °C (lit.⁷ mp 185-1187 °C).

^1H NMR (300 MHz, CDCl_3) $\delta = 7.83$ (d, $J = 8.4$ Hz, 4 H, ArH), 7.25 (d, $J = 8.4$ Hz, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 136.37, 134.94, 133.13, 109.69, 121.62$ (q, $J_{\text{CF}} = 367.8$ Hz, SO_2CF_3), 21.4.

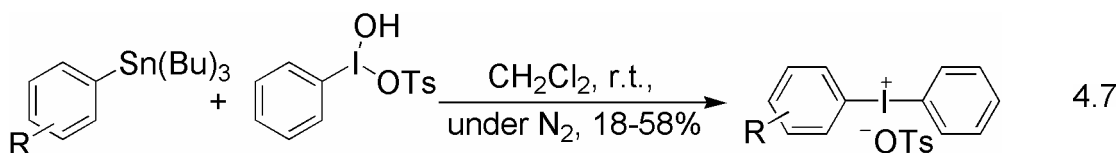
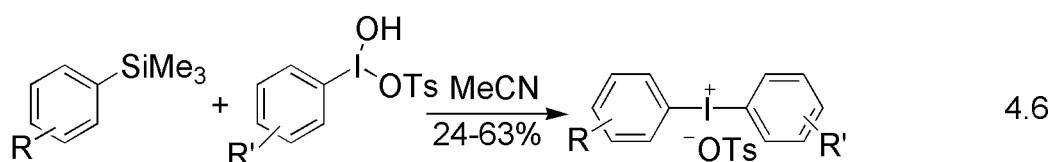
d. References

1. Hossain, M. D.; Kitamura, T. *Bull. Chem. Soc. Jpn.* **2006**, 79, 142.
2. Hossain, M. D.; Kitamura, T. *Tetrahedron* **2006**, 62, 6955.
3. Ye, C.; Twamley, B.; Shreeve, J. M. *Org. Lett.* **2005**, 7, 3961.
4. a) Zupan, M.; Iskra, J.; Stavber, S. *Tetrahedron Lett.* **1997**, 38, 6305. b) Stavber, S.; Jereb, M.; Zupan, M. *Chem. Commun.* **2002**, 488. c) Pavlinac, J.; Zupan, M.; Stavber, S. *J. Org. Chem.* **2006**, 71, 1027.
5. Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, 55, 639.
6. Vogel, D.; Vogel, K. M. *Eur. Pat. Appl.* **1996**, 8pp.
7. Stang, P. J.; Zhdankin, V. V.; Tykwinski, R.; Zefirov, N. S. *Tetrahedron Lett.* **1991**, 32, 7497.
8. Nagai, T.; Goto, K. *Jpn. Kokai Tokkyo Koho* **2004**, 18pp.
9. Miller, R. D. U.S., 4786441, 22 Nov 1988.
10. Kitamura, T.; Matsuyuki, J.; Nagata, K.; Furuki, R.; Taniguchi, H. *Synthesis* **1992**, 945.

C. Straightforward Synthesis of Diaryliodonium Salts Using Potassium Peroxodisulfate

a. Introduction

There are many methods for the preparation of diaryliodonium salts,¹ but very few of them involve the syntheses of diaryliodonium triflate and tosylate salts. Most of the diaryliodonium triflates and tosylates have been prepared from (diacetoxyiodo)arenes because of their stability and easy handling. For example, (a) diaryliodonium triflates are prepared by the reaction of aromatic substrates with (diacetoxyiodo)benzene activated by triflic acid or trifluoroacetic acid.^{2,3} For the synthesis of diaryliodonium tosylates (eq. 4.6 and 4.7),^{4,5} the preparative methods involve the reaction of [hydroxy(tosyloxy)iodo]arenes, which are prepared from (diacetoxyiodo)arenes. Therefore, once (diacetoxyiodo)arenes are available, diaryliodonium triflates and tosylates can be readily prepared.

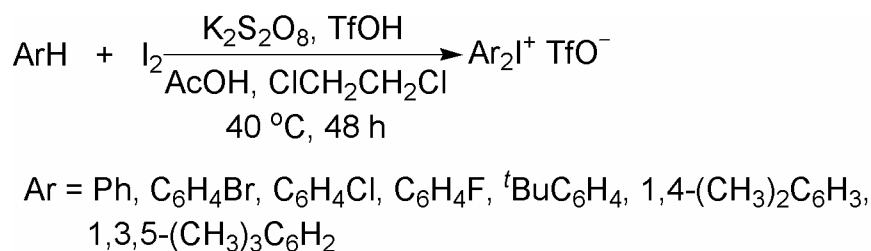


The most ideal procedure for diphenyliodonium triflate should involve a straightforward synthesis from benzene and iodine. This procedure gives the direct and efficient method that does not contain the step via iodobenzene synthesis. Preparation of diaryliodonium triflates

has been studied so far by using $\text{ArI}(\text{OAc})_2$.^{2,3} Diaryliodonium triflates are directly prepared by the reaction of arenes and iodine in the presence of $\text{K}_2\text{S}_2\text{O}_8$ in TFA, followed by treatment with NaOTf which have already described in chapter IV (B).⁶ However, this method requires two successive procedures to obtain triflate salts: (1) reaction of arenes and iodine, and (2) exchange of the counter anion with triflate. Herein, a one-pot, easy method for the preparation of diaryliodonium triflates from arenes and iodine is reported. Also a one-pot, easy method for the preparation of diaryliodonium tosylates from arenes and iodine is described.

b. Results and Discussion

Generally, (diacetoxyiodo)arenes are activated by adding a strong acid and react with arenes to give diaryliodonium salts. As the strong acid exists in the preparation of (diacetoxyiodo)arenes, it is expected that diaryliodonium salts are formed by the reaction of the in situ generated (diacetoxyiodo)arenes on using excess aromatic substrates. Thus, one-pot preparation of diaryliodonium triflates, $\text{Ar}_2\text{I}^+\text{OTf}^-$, and tosylates, $\text{Ar}_2\text{I}^+\text{OTs}^-$, from arenes and iodine were examined by applying the previous method (Chapter II, D). In the case of diphenyliodonium triflate, the reaction of benzene with elemental iodine was conducted in AcOH with triflic acid in the presence of commercial $\text{K}_2\text{S}_2\text{O}_8$ as the oxidant at 40 °C. This simple, one-pot reaction for 48 h gave diphenyliodonium triflate directly in 72% yield (Table 4.5, entry 1). In order to explore the scope of this reaction, it was applied to other aromatic substrates. The outline is shown in Scheme 4.7. The results are given in Table 4.5.



Scheme 4.7

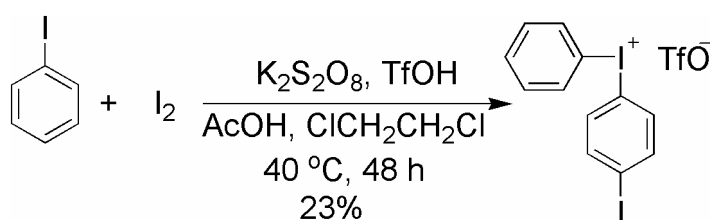
Table 4.5 Preparation of Diaryliodonium Triflates from Arenes^a

Entry	Arene	Product	Yield (%)
1	Benzene	Ph ₂ I ⁺ TfO ⁻	72
2 ^b	Benzene	Ph ₂ I ⁺ TfO ⁻	71
3	Bromobenzene	(4-BrC ₆ H ₄) ₂ I ⁺ TfO ⁻	55
4	Chlorobenzene	(4-ClC ₆ H ₄) ₂ I ⁺ TfO ⁻	60
5	Fluorobenzene	(4-FC ₆ H ₄) ₂ I ⁺ TfO ⁻	68
6	<i>tert</i> -Butylbenzene	(4- ^t BuC ₆ H ₄) ₂ I ⁺ TfO ⁻	81
7	<i>p</i> -Xylene	(2,5-Me ₂ C ₆ H ₃) ₂ I ⁺ TfO ⁻	47
8	Mesitylene	(2,4,6-Me ₃ C ₆ H ₂) ₂ I ⁺ TfO ⁻	56

^aThe reaction of an arene (10 mmol) was carried out in AcOH (5 mL), TfOH (10 mmol), 1,2-dichloroethane (2 mL) and iodine (0.52 mmol) in the presence of K₂S₂O₈ (5.11 mmol) at 40 °C for 48 h. ^bBenzene (100 mmol), AcOH (50 mL), TfOH (100 mmol), 1,2-dichloroethane (20 mL), and iodine (5.2 mmol) and K₂S₂O₈ (51.1 mmol).

The preparation of diphenyliodonium triflate from benzene can be easily scaled up (Table

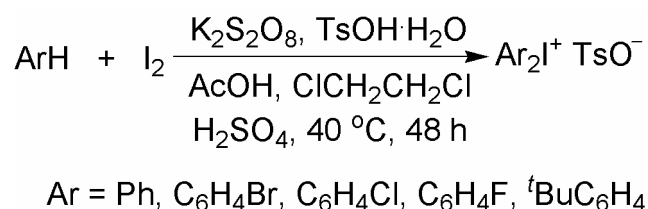
4.5, entry 2), together with the complete absence of effluent or byproduct problems. Arenes bearing weakly deactivated groups such as bromo, chloro and fluoro groups gave diaryliodonium triflates in good yields (Table 4.5, entries 3-5). However, the similar reaction of iodobenzene did not give bis(4-iodophenyl)iodonium triflate but afforded (4-iodophenyl)(phenyl)iodonium triflate in 23% yield (Scheme 4.8). In the reaction of iodobenzene, it is considered that the iodo group of iodobenzene is oxidized to form (diacetoxyiodo)benzene, which reacts with iodobenzene to yield the (4-iodophenyl)(phenyl)iodonium salt, as it is observed previously in the reaction of iodobenzene (Chapter IV, A).⁷ *tert*-Butylbenzene, *p*-xylene, and mesitylene gave bis(4-*tert*-butylphenyl)iodonium triflate, bis(2,5-dimethylphenyl)iodonium triflate, and bis(2,4,6-trimethylphenyl)iodonium triflate, respectively (Table 4.5, entries 6-8). This method was not applicable for arenes with strong electron-donating groups. For example, in the case of anisole, the reaction mixture was quickly oxidized to indicate black color, but no diaryliodonium salts were obtained. This method was not effective for arenes with strong electron-withdrawing groups such as trifluoromethyl and nitro groups due to their decreased reactivity.



Scheme 4.8

Similarly, it was applied to the synthesis of diaryliodonium tosylates, Ar₂I⁺TsO⁻. Diphenyliodonium tosylate, Ph₂I⁺OTs⁻, was prepared from benzene with iodine in the presence of AcOH, H₂SO₄, 1,2-dichloroethane and *p*-toluenesulfonic acid monohydrate with

K₂S₂O₈ at 40 °C. In order to explore the scope of this reaction, it was applied to other aromatic substrates. The outline is shown in Scheme 4.9. The results are given in Table 4.6. Arenes bearing weakly deactivated groups such as bromo, chloro, and fluoro groups gave diaryliodonium tosylates (Table 4.6, entries 3-5). *tert*-Butylbenzene gave bis(4-*tert*-butylphenyl)iodonium tosylate in good yield (Table 4.6 entry 6). This method was not applicable for electron-rich arenes such as anisole, mesitylene, and *p*-xylene. This method was not effective for arenes with strong electron-withdrawing groups such as trifluoromethyl and nitro groups due to their decreased reactivity.



Scheme 4.9

Table 4.6 Preparation of Diaryliodonium Tosylates from Arenes^a

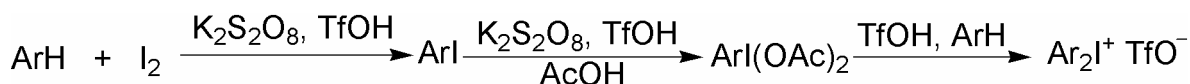
Entry	Arene	Product	Yield (%)
1	Benzene	Ph ₂ I ⁺ TsO ⁻	67
2 ^b	Benzene	Ph ₂ I ⁺ TsO ⁻	65
3	Bromobenzene	(4-BrC ₆ H ₄) ₂ I ⁺ TsO ⁻	22
4	Chlorobenzene	(4-ClC ₆ H ₄) ₂ I ⁺ TsO ⁻	24
5	Fluorobenzene	(4-FC ₆ H ₄) ₂ I ⁺ TsO ⁻	50
6	<i>tert</i> -Butylbenzene	(4- <i>t</i> BuC ₆ H ₄) ₂ I ⁺ TsO ⁻	85

^aThe reaction of an arene (10 mmol) was carried out in AcOH (5 mL), TsOH (2.36 mmol), H₂SO₄ (8

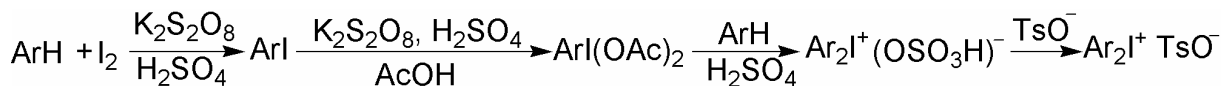
mmol), 1,2-dichloroethane (2 mL) and iodine (0.52 mmol) in the presence of K₂S₂O₈ (5.11 mmol) at 40 °C for 48 h.

^bBenzene (100 mmol), AcOH (50 mL), TsOH (23.6 mmol), H₂SO₄ (80 mmol), 1,2-dichloroethane (20 mL), and iodine (5.2 mmol) and K₂S₂O₈ (51.1 mmol).

In the formation of diaryliodonium triflates, it is considered that there exist three major steps: iodination of arenes, diacetoxylation of iodoarenes, and arylation of (diacetoxyiodo)arenes (Scheme 4.10). The key step is the formation of (diacetoxyiodo)arenes. As it is discussed in Chapter II (D), the formation of (diacetoxyiodo)arenes is an efficient process from arenes and iodine promoted by K₂S₂O₈. It is considered that once (diacetoxyiodo)arenes are formed, they are immediately activated by TfOH to react with excess aromatic compounds and provide diaryliodonium triflates.² In the case of diaryliodonium tosylates, the reaction proceeds with the similar process to the formation of diaryliodonium triflates (Scheme 4.11). However, (diacetoxyiodo)arenes are activated by H₂SO₄ and react with excess arenes to yield diaryliodonium sulfates. Finally, anion exchanges with tosylate.



Scheme 4.10



Scheme 4.11

The present methods described above cover relatively electron-rich to weakly deactivated aromatic substrates. This method involves fundamental starting materials (simple arenes, elemental iodine, and commercial K₂S₂O₈). The simple and convenient one-pot procedures for

diaryliodonium triflates and tosylates have a significant advantage over the previous reported ones (Chapter IV, B).

c. Experimental Section

Optimized Procedure for Preparing Diaryliodonium Triflates from Arenes

A solution of an appropriate arene (10 mmol) in a mixture of molecular iodine (0.52 mmol), AcOH (5 mL), TfOH (10 mmol) and 1,2-dichloroethane (2 mL) was heated with stirring to 40 °C. After dissolving iodine, K₂S₂O₈ (5.11 mmol) was added. The reaction mixture was stirred at that temperature for 48 h. After completion of the reaction, water (12 mL) was added. The resulting precipitates were collected by filtration under reduced pressure, washed with CH₂Cl₂ (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with CH₂Cl₂ (4×10 mL), followed by drying (anhydrous Na₂SO₄), filtration, and removal of the solvent by evaporation. The crude product was washed with Et₂O (3×3 mL), and recrystallized from CH₂Cl₂/hexane.

Large scale synthesis (Table 4.5, Entry 2) was conducted for diphenyliodonium triflate in a similar manner. A mixture of benzene (7.8 g, 100 mmol), AcOH (50 mL), 1,2-dichloroethane (20 mL), TfOH (100 mmol) and I₂ (1.32 g, 5.2 mmol) was heated with stirring to 40 °C. After dissolving iodine, K₂S₂O₈ (51.1 mmol) was added and the stirring was continued 48 h. Workup of the reaction mixture gave pure product (3.16 g, 71%).

Diphenyliodonium triflate

Yield: 0.324 g (72%); mp 177-178 °C (lit.⁸ mp 178-180 °C).

¹H NMR (300 MHz, CDCl₃) δ = 8.19 (d, *J* = 8.1 Hz, 4 H, ArH), 7.66 (t, *J* = 8.1 Hz, 2 H, ArH), 7.51 (t, *J* = 8.1 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 136.39, 133.56, 133.10, 121.78 (q, J_{CF} = 316.5 Hz, SO_2CF_3), 115.80.

Bis(4-bromophenyl)iodonium triflate

Yield: 0.334 g (55%); mp 190-191 °C (lit.⁹ mp 198 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.12 (d, J = 8.4 Hz, 4 H, ArH), 7.67 (d, J = 8.4 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 138.12, 136.24, 128.69, 121.73 (q, J_{CF} = 316.42 Hz, SO_2CF_3), 114.25.

Bis(4-chlorophenyl)iodonium triflate¹⁰

Yield: 0.294 g (60%); mp 175-176 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.21 (d, J = 8.7 Hz, 4 H, ArH), 7.53 (d, J = 8.7 Hz, 4 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 140.41, 138.08, 133.22, 121.74 (q, J_{CF} = 316.5 Hz, SO_2CF_3), 113.55.

Bis(4-fluorophenyl)iodonium triflate¹¹

Yield: 0.332 g (68%); mp 167-168 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.25-8.21 (m, 4 H, ArH), 7.31 (t, J = 8.7 Hz, 4 H, ArH).

^{13}C NMR (75MHz, CDCl_3) δ = 166.35 (d, J_{CF} = 252.22 Hz, CF), 139.31 (d, J_{CF} = 9.3 Hz, CCF), 121.78 (q, J_{CF} = 316.5 Hz, SO_2CF_3), 120.50 (d, J_{CF} = 23.47 Hz, CCF), 110.11.

Bis(4-*tert*-butylphenyl)iodonium triflate¹²

Yield: 0.453 g (81%); mp 164-165 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.11 (d, J = 8.4 Hz, 4 H, ArH), 7.54 (d, J = 8.4 Hz, 4 H, ArH), 1.28 (s, 18H, Me).

^{13}C NMR (75 MHz, CDCl_3) δ = 157.61, 136.15, 130.39, 121.78 (q, J_{CF} = 317.1 Hz, SO_2CF_3), 35.99, 31.32.

(4-iodophenyl)(phenyl)iodonium triflate

Yield: 1.27 g (23%) mp 138-140 °C (lit.¹³ mp 144-148 °C).

^1H NMR (300 MHz, CDCl_3) δ = 8.18 (d, J = 8.4 Hz, 2 H, ArH), 7.91 (q, J = 8.4 Hz, 4 H, ArH), 7.68 (t, J = 8.4 Hz, 1 H, ArH), 7.55 (t, J = 8.4 Hz, 2 H, ArH).

^{13}C NMR (75 MHz, CDCl_3) δ = 142.29, 137.75, 136.47, 133.77, 133.24, 121.79 (q, J_{CF} = 315.9 Hz, SO_2CF_3), 116.07, 115.16, 100.61.

Bis(2,4-dimethylphenyl)iodonium triflate

Yield: 0.238 g (47%); mp 192-193 °C.

^1H NMR (300 MHz, CDCl_3) δ = 8.02 (s, 2 H, ArH), 7.41 (s, 4 H, ArH), 2.59 (s, 6 H, Me), 2.35 (s, 6 H, Me).

^{13}C NMR (75 MHz, CDCl_3) δ = 141.40, 139.22, 138.28, 135.07, 132.63, 121.79 (q, J_{CF} = 315.8 Hz, SO_2CF_3), 119.4, 24.98, 20.45.

Anal. Found: C, 41.91; H, 3.72%. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{IF}_3\text{S}$: C, 41.98; H, 3.70%.

Bis(2,4,6-trimethylphenyl)iodonium triflate

Yield: 0.298 g (56%); mp 190-192 °C (lit.⁹ mp 192-193 °C).

^1H NMR (300 MHz, CDCl_3) δ = 7.19 (s, 4 H, ArH), 2.53 (s, 12 H, Me), 2.34 (s, 6 H, Me).

^{13}C NMR (75 MHz, CDCl_3) δ = 145.20, 143.55, 133.74, 121.76 (q, J_{CF} = 316.42 Hz, SO_2CF_3), 118.94, 26.09, 20.84.

Optimized Procedure for Preparing Diaryliodonium Tosylates from Arenes

A solution of an appropriate arene (10 mmol) in a mixture of molecular iodine (0.52 mmol), AcOH (5 mL), H_2SO_4 (8 mmol), TsOH (2.36 mmol) and 1,2-dichloroethane (2 mL) was

heated with stirring to 40 °C. After dissolving iodine, K₂S₂O₈ (5.11 mmol) was added. The reaction mixture was stirred at that temperature for 48 h. After completion of the reaction, water (12 mL) was added. The resulting precipitates were collected by filtration under reduced pressure, washed with CH₂Cl₂ (10 mL), and discarded. The crude product was obtained by extraction of the filtrate with CH₂Cl₂ (4×10 mL), followed by drying (anhydrous Na₂SO₄), filtration and removal of the solvent by evaporation. The crude product was washed with Et₂O (3×3 mL), and recrystallized from CH₂Cl₂/hexane.

Large scale synthesis (Table 4.6, Entry 2) was conducted for diphenyliodonium tosylate in a similar manner. A solution of benzene (7.8 g, 100 mmol) in a mixture of AcOH (50 mL), 1,2-dichloroethane (20 mL), H₂SO₄ (80 mmol), TsOH (23.6 mmol) and I₂ (1.32 g, 5.2 mmol) was heated with stirring to 40 °C. After dissolving iodine, K₂S₂O₈ (51.1 mmol) was added and the stirring was continued 48 h. Workup of the reaction mixture gave pure product (3.07 g, 65%).

Diphenyliodonium tosylate

Yield: 0.313 g (67%); mp 178-179 °C (lit.⁵ mp 179-180 °C).

¹H NMR (300 MHz, CDCl₃) δ = 8.14 (d, *J* = 8.1 Hz, 4 H, ArH), 7.68 (d, *J* = 8.1 Hz, 2 H, ArH), 7.62 (t, *J* = 8.1 Hz, 2 H, ArH), 7.47 (t, *J* = 8.1 Hz, 4 H, ArH), 7.17 (d, *J* = 8.1 Hz, 2 H, ArH), 2.31 (s, 3 H, Me).

¹³C NMR (75 MHz, CDCl₃) δ = 143.67, 141.52, 136.39, 133.44, 133.04, 129.78, 126.9 115.98, 21.31.

Bis(4-bromophenyl)iodonium tosylate

Yield: 0.137 g (22%); mp 200-201 °C (lit.¹⁴ mp 203 °C).

¹H NMR (300 MHz, CDCl₃) δ = 8.06 (d, *J* = 8.4 Hz, 4 H, ArH), 7.66 (d, *J* = 8.4 Hz, 6 H,

ArH), 7.20 (d, $J = 8.4$ Hz, 2 H, ArH), 2.36 (s, 3 H, Me).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 141.64, 138.15, 136.25, 133.92, 129.82, 128.66, 126.93, 114.50, 21.34$.

Bis(4-chlorophenyl)iodonium tosylate¹⁵

Yield: 0.131 g (24%); mp 205-206 °C.

^1H NMR (300 MHz, CDCl_3) $\delta = 8.14$ (d, $J = 7.8$ Hz, 4 H, ArH), 7.65 (d, $J = 7.8$ Hz, 2 H, ArH), 7.49 (d, $J = 7.8$ Hz, 4 H, ArH), 7.20 (d, $J = 7.8$ Hz, 2 H, ArH), 2.35 (s, 3 H, Me).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 141.66, 140.37, 138.11, 137.33, 133.24, 129.82, 126.92, 113.78, 21.32$.

Bis(4-fluorophenyl)iodonium tosylate

Yield: 0.255 g (50%); mp 189-190 °C.

^1H NMR (300 MHz, CDCl_3) $\delta = 8.22$ (s, 4 H, ArH), 7.67 (d, $J = 7.2$ Hz, 2 H, ArH), 7.25-7.2 (m, 6H, ArH), 2.34 (s, 3 H, Me).

^{13}C NMR (75MHz, CDCl_3) $\delta = 166.20$ (d, $J_{\text{CF}} = 252.22$ Hz, CF), 143.60, 141.64, 139.33 (d, $J_{\text{CF}} = 9.22$ Hz, CCF), 129.83, 126.91, 120.39 (d, $J_{\text{CF}} = 22.87$ Hz, CCF), 110.33, 21.3.

Anal. Found: C, 46.64; H, 3.04%. Calcd for $\text{C}_{19}\text{H}_{15}\text{O}_3\text{IF}_2\text{S}$: C, 46.73; H, 3.07%.

Bis(4-*tert*-butylphenyl)iodonium tosylate¹⁶

Yield: 0.495 g (85%); mp 250-251 °C.

^1H NMR (300 MHz, CDCl_3) $\delta = 8.06$ (d, $J = 7.8$ Hz, 4 H, ArH), 7.69 (d, $J = 7.8$ Hz, 2 H, ArH), 7.51 (d, $J = 7.8$ Hz, 4 H, ArH), 7.18 (d, $J = 7.8$ Hz, 2 H, ArH), 1.28 (s, 18H, Me).

^{13}C NMR (75 MHz, CDCl_3) $\delta = 157.52, 141.70, 141.47, 136.18, 130.36, 129.78, 126.97, 112.48, 36.03, 31.35, 21.36$.

d. References

1. a) Zefirov, N. S.; Kasumov, T. M.; Koz'min, A. S.; Sorokin, V. D.; Stang, P. J.; Zhdankin, V. V. *Synthesis* **1993**, 1209. b) Beringer, F. M.; Dresler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* **1953**, 75, 2705. c) Beringer, F. M.; Falk, R. A.; Karniol, M.; Lillien, I.; Masullo, G.; Mausner, M.; Sommer, E. *J. Am. Chem. Soc.* **1959**, 81, 342. d) Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1972**, 37, 1516. e) Tyrra, W.; Butter, H.; Naumann, D. *J. Fluorine Chem.* **1993**, 60, 79. f) Beringer, F. M.; Dehn, J. W.; Winicov, M. *J. Am. Chem. Soc.* **1960**, 82, 2948. g) Schmeisser, M.; Dahmen, K.; Sartori, P. *Chem. Ber.* **1970**, 103, 307. h) Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Heterocycl. Chem.* **1992**, 29, 815. i) Beringer, F. M.; Lillien, I. *J. Am. Chem. Soc.* **1960**, 82, 725. j) Kasumov, T. M.; Brel, V. K.; Kozmin, A. S.; Zefirov, N. S. *Synthesis* **1995**, 775.
2. Kitamura, T.; Matsuyuki, J.; Taniguchi, H. *Synthesis* **1994**, 147.
3. Shah, A.; Pike, V. W.; Widdowson, D. A. *J. Chem. Soc. Perkin Trans. 1* **1997**, 2463.
4. Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, 45, 1543.
5. Pike, V. W.; Butt, F.; Shah, A.; Widdowson, D. A. *J. Chem. Soc. Perkin Trans. 1* **1999**, 245.
6. Hossain, M. D.; Ikegami, Y.; Kitamura, T. *J. Org. Chem.* **2006**, 71, 9903.
7. Hossain, M. D.; Kitamura, T. *Tetrahedron* **2006**, 62, 6955.
8. Dektar, J. L.; Hacker, N. P. *J. Org. Chem.* **1990**, 55, 639.
9. Stang, P. J.; Zhdankin, V. V.; Tykwinski, R.; Zefirov, N. S. *Tetrahedron Lett.* **1991**, 32, 7497.
10. Vogel, D.; Vogel, K. M. *Eur. Pat. Appl.* **1996**, 8pp.
11. Nagai, T.; Goto, K. *Jpn. Kokai Tokkyo Koho* **2004**, 18pp.
12. Miller, R. D. U.S., 4786441, 22 Nov 1988.
13. Kitamura, T.; Matsuyuki, J.; Nagata, K.; Furuki, R.; Taniguchi, H. *Synthesis* **1992**, 945.

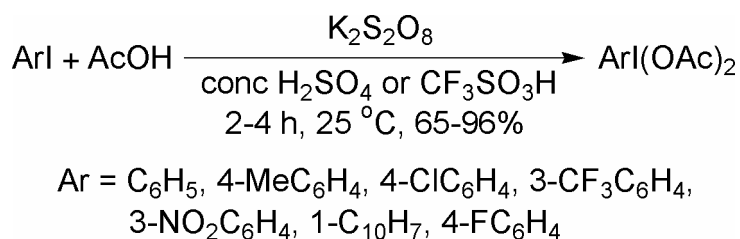
14. Johannes, E.; Carsten, H.; Thomas, L.; Rene, G.; Heinz, H. C. *J. Labelled Comps. & Radiopharm.* **2004**, 47, 429.
15. David, B. H.; Michael, J. S. *Ger. Offen.* **1976**, 36pp.
16. Kyoichi, T.; Shinji, I. *PCT Int. Appl.* **2001**, 55pp.

Chapter V

Summary and Concluding Remarks

Hypervalent organoiodine (III) compounds prepared newly in this dissertation are classified into three types: (diacetoxyiodo)arenes (Chapter II), [bis(trifluoroacetoxy)iodo]arenes (Chapter III), diaryliodonium salts (Chapter IV). Eight novel preparative methods of reactive hypervalent iodine compounds have been presented by using different conditions. The results described in this thesis are important not only in synthetic organic chemistry but also in hypervalent iodine chemistry. The results obtained in this study are summarized as follows:

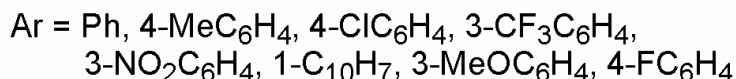
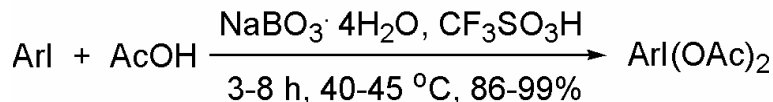
1. A novel (or considerably improved) preparative procedure has been developed, which is easy, quick, cheap and possibly environmentally benign. The new method gave (diacetoxyiodo)arenes in high yields by the reaction of iodoarenes with $K_2S_2O_8$ in AcOH in the presence of concd H_2SO_4 or CF_3SO_3H at room temperature within short time (Scheme 5.1). This procedure avoided the use of high temperature and the severe reaction conditions.



Scheme 5.1

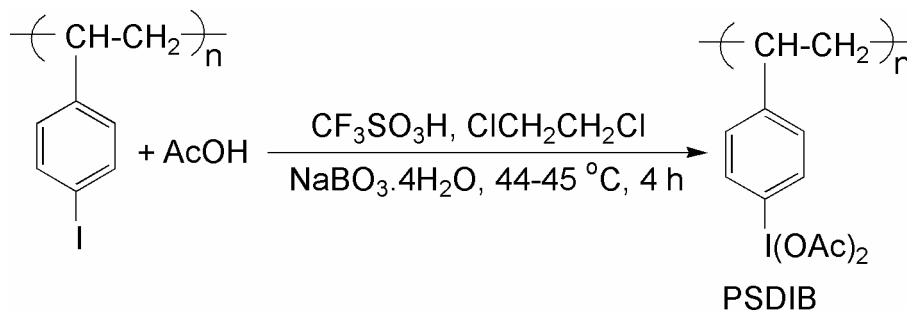
2. The reaction of the iodoarenes with sodium perborate in acetic acid in the presence of trifluoromethanesulfonic (triflic acid) at 40-45 °C, efficiently generated the corresponding

(diacetoxyiodo)arenes in high yields within short time (Scheme 5.2). Addition of triflic acid as a promoter causes a drastic increase in the yield of (diacetoxyiodo)arenes in the reaction of iodoarenes with sodium perborate.



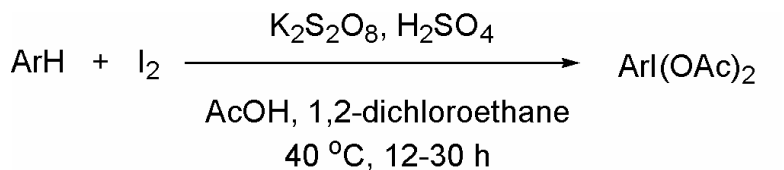
Scheme 5.2

3. An operationally simple, and efficient considerably improved preparative procedure of poly[4-(diacetoxyiodo)styrene] (PSDIB) was reported, using poly(4-iodostyrene)/AcOH/ClCH₂CH₂Cl/CF₃SO₃H/ NaBO₃ system (Scheme 5.3). The product can serve as an improved and recyclable oxidant for modern organic synthesis and particularly in combinatorial chemistry.



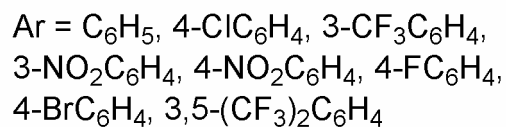
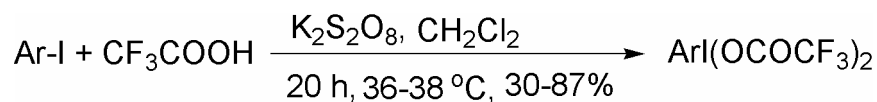
Scheme 5.3

4. The reaction of arenes with potassium peroxodisulfate, elemental iodine and acetic acid in the presence of concd sulfuric acid, efficiently afforded the corresponding (diacetoxyiodo)arenes in good yields (Scheme 5.4). The presented (diacetoxyiodo)arenes can be safely scaled up.



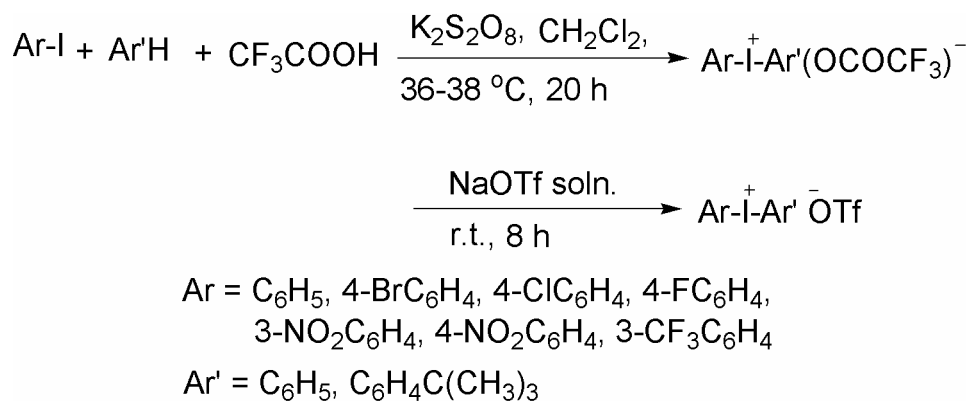
Scheme 5.4

5. A new (or considerably improved) preparative procedure presented, which is easy, cheap and possibly environmentally benign. The new method formed [bis(trifluoroacetoxy)iodo]arenes in high yields by the reaction of iodoarenes with K₂S₂O₈ in CF₃CO₂H and CH₂Cl₂ at 36-38 °C (Scheme 5.5).



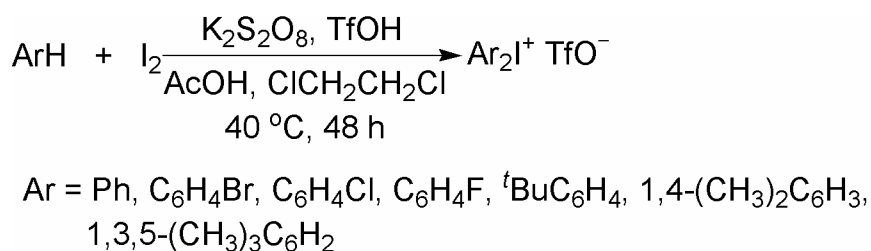
Scheme 5.5

6. Diaryliodonium triflates have been directly prepared by reaction of some iodoarenes with aromatic substrates in good yields by using K₂S₂O₈/CF₃COOH/CH₂Cl₂ system (Scheme 5.6). Treatment of a variety of iodoarenes with iodobenzene under the same conditions resulted in ligand transfer, and (4-iodophenyl)(phenyl)iodonium triflate was obtained.



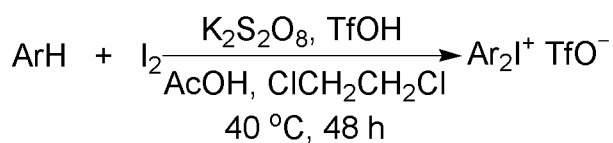
Scheme 5.6

7. The new method gave diaryliodonium triflates in good yields by the reaction of arenes with elemental iodine, K₂S₂O₈, CF₃COOH and ClCH₂CH₂Cl at 40 °C (Scheme 5.7). This procedure avoided the use of high temperature and the severe reaction conditions. The presented diaryliodonium triflates can be safely scaled up.



Scheme 5.7

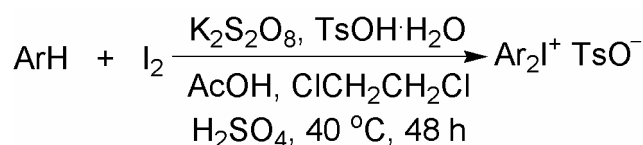
8. Diaryliodonium triflates prepared in good yields by the reaction of arenes with elemental iodine, K₂S₂O₈, AcOH, TfOH and ClCH₂CH₂Cl at 40 °C (Scheme 5.8). The new method also gave diaryliodonium tosylates by the reaction of arenes with elemental iodine, K₂S₂O₈, AcOH,



Ar = Ph, C₆H₄Br, C₆H₄Cl, C₆H₄F, ^tBuC₆H₄, 1,4-(CH₃)₂C₆H₃,
1,3,5-(CH₃)₃C₆H₂

Scheme 5.8

H₂SO₄, TsOH and ClCH₂CH₂Cl at 40 °C (Scheme 5.9). This procedure involved mild conditions and straightforward one-pot synthesis.



Ar = Ph, C₆H₄Br, C₆H₄Cl, C₆H₄F, ^tBuC₆H₄

Scheme 5.9

Since the report by Willgerodt on (dichloroiodo)benzene as the first hypervalent organoiodine (III) compound in 1886, a lot of organic chemists have prepared the several types of hypervalent organoiodine (III) compounds and the number of hypervalent iodonium compounds come to more than 4800 from 1967 to date. Hypervalent iodine compounds have attracted increasing interest as green oxidants in organic synthesis due to their low toxicity, ready availability, easy handling, high efficiency, stability to air and moisture, and economical alternative to heavy metal reagents such as lead(IV), thallium(III), and mercury(II). Although the history of the hypervalent iodine chemistry and the utilization of hypervalent iodine reagents to synthetic reactions are still in a fundamental stage, hypervalent iodine-mediated reactions have been developed extensively in the past twenty years and will be developed more and more in a future. It is my great pleasure if the results described in this thesis can contribute to the organic synthetic chemistry and also to the hypervalent iodine chemistry.

In the further research, the author pursues the preparation of novel hypervalent iodine (III) reagents containing alkenyl and alkynyl iodonium salts, polynuclear aromatic compounds or several substituents and application to organic synthesis.

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