



Review Article

APPLICATION OF HYPERVALENT IODINE COMPOUNDS IN ADVANCED GREEN TECHNOLOGIES

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Abstract

This review summarizes industrial applications of inorganic and organic polyvalent (hypervalent) iodine compounds. Inorganic iodate salts have found some application as a dietary supplements and food additives. Iodine pentafluoride is used as industrial fluorinating reagent, and iodine pentoxide is a powerful and selective oxidant that is particularly useful in analytical chemistry. Common organic hypervalent iodine reagents such as (dichloroiodo)benzene and (diacetoxyiodo)benzene are occasionally used in chemical industry as the reagents for production of important pharmaceutical intermediates. Iodonium salts have found industrial application as photoinitiators for cationic photopolymerizations. Various iodonium compounds are widely used as precursors to [¹⁸F]-fluorinated radiotracers in the Positron Emission Tomography (PET).

Keywords: Iodine, applications of iodine, hypervalent iodine, photoinitiators, photoacid generators, green chemistry, Positron Emission Tomography.

1. Introduction

Iodine is an essential for our life element with many practical applications. It is not a very common element, ranking number 61 by abundance on Earth out of 96 stable elements [1]. However, there are enormous sources of iodine concentrated in seaweeds, underground brines, and caliche ores. According to Statista.com, global iodine production of iodine in 2020 was 30,000 metric tons, remaining at about the same annual level for the last ten years [2]. About 60 % of iodine is produced from caliche ores in Chile, which has estimated reserves 1,800,000 tons. The iodine reserves in underground brines in numerous countries (Japan, USA, Russia, Indonesia, Turkmenistan, Azerbaijan, and Russia) are estimated at about 6,000,000

tons [1]. Current average bulk price of iodine varies within the range of \$10–20 per kg.

Iodine and iodine compounds have found numerous applications in medicine and industry [3]. Iodine use is closely linked to our daily life. Elemental iodine is commonly used as a disinfectant, such as, tincture of iodine. Iodine compounds are used in X-ray contrast media and as disinfectants in medical and sanitary fields. Iodine has numerous applications in industry and agriculture. Ethylenediamine dihydroiodide is a nutritional supplement for livestock, and its production consumes a large fraction of available iodine. Recently, demand for iodine has grown in high technology fields where it is employed in LCD polarizing film and etching agents for semiconductors, as well as in solar cells and laser equipment.

About 16% of iodine world production is used in industrial catalysis. A catalytic cycle involving generation of organic iodides is utilized in the important Monsanto-Cativa industrial process for the produc-

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tion of acetic acid. In this process, the catalytic hydroiodic acid converts the methanol feedstock into methyl iodide, which undergoes Rh- or Ir-catalyzed carbonylation. Hydrolysis of the resulting acetyl iodide regenerates hydroiodic acid and gives acetic acid [4]. The carbonylation of methanol, catalyzed by rhodium in the presence of hydroiodic acid, was originally invented by Monsanto company in the 1960s. In the 1990s, Eastman Chemical company developed a modification of this industrial process based on the use of lithium iodide as the co-catalyst [5]. Iodine is widely used as radical initiator and catalyst in production of various polymers [3].

In natural organic compounds and in the human body, iodine occurs exclusively in the monovalent state. However, it can form various polyvalent compounds in different oxidation states. Compounds of polyvalent iodine are commonly referred to as “hypervalent” iodine compounds, which reflects the special [3c–4e] hypervalent bonding present in these molecules [6]. Structural features and reactivity pattern of hypervalent iodine compounds in many aspects are similar to the derivatives of heavy transition metals [7]. Reactions of iodine compounds are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination, and ligand coupling, which are typical of the transition metal chemistry. In contrast to the heavy metals, iodine is an environmentally friendly and a relatively inexpensive element. Organic compounds of polyvalent iodine have emerged as versatile, efficient and environmentally friendly synthetic reagents with numerous applications in academic and industrial research [8]. Hypervalent iodine compounds are widely used as mild and selective oxidants and electrophilic group transfer reagents in organic synthesis. Iodonium salts have found widespread industrial application as initiators of polymerization [9], as well as precursors to [18F]-fluorinated radiotracers in the Positron Emission Tomography (PET) [10]. The present review provides a summary of industrial applications of inorganic and organic polyvalent iodine compounds with emphasis on the applications of iodonium salts.

2. Methodological Section

Iodate salts are the most thermodynamically stable inorganic derivatives of polyvalent iodine [7]. Potassium iodate, KIO_3 , has found some application in food industry as a dietary supplement and a food additive. In particular, it is used as a source of iodine in

iodized salt, and also as a dough conditioner [11]. Potassium iodate is more stable than KI in the presence of air, and therefore it is the preferable iodine additive to salt for correcting iodine deficiency. Iodate is quickly reduced to iodide in human body providing essential for thyroid function iodine. High levels of iodate above 0.600 mg/day may damage human eyes [12]. However, with the average iodate content in iodized salt (28 to 110 mg of KIO_3 per kilogram of salt) and the daily salt consumption of 15 g, this results in a human exposure of 440 to 1700 μg of iodate per day, which is significantly below the toxicity levels. The toxicology data indicate a negligible risk of consumption iodate-fortified salt.

Metal iodates belong to a particularly important class of the second-order nonlinear optical (NLO) materials [13]. NLO materials are used in photonic technologies, including laser frequency conversion, optical parameter oscillator (OPO), and signal communication. Lithium iodate is one of the most important and commercially manufactured representatives of NLO materials [13]. Several iodate salts including $\alpha\text{-LiIO}_3$, NaI_3O_8 [14], and $\alpha\text{-Cs}_2\text{I}_4\text{O}_{11}$ [15], are promising thermally stable Second Harmonic Generation (SHG) materials characterized by large SHG coefficients, wide transparent wavelength regions, and high optical-damage thresholds.

Iodine pentoxide (I_2O_5), the most stable halogen oxide, has found practical application as a powerful and selective oxidant which is particularly useful in analytical chemistry. Iodine pentoxide is a unique reagent that can completely oxidize carbon monoxide at room temperature. This reaction is used as analytical method for measuring the concentration of carbon monoxide in gaseous mixtures [16].

Periodic acid (HIO_4 or H_5IO_6) and periodates are powerful oxidants. Periodic acid in acidic solution is a unique oxidant that can rapidly and quantitatively convert manganese(II) to manganese(VII) [16]. It can selectively cleave carbon-carbon bond in glycols and related organic compounds such as α -diketones, α -ketols, α -aminoalcohols, and α -diamines. Periodate oxidation reactions are widely employed in the chemistry of carbohydrates and nucleic acids. Oxidations with periodic acid and periodates are commonly used in chemical and instrumental methods of analysis of polysaccharides [17], oligosaccharides [18], glycosides [19], glycoproteins [20], and other organic products of biological origin. The use of periodate oxidation in instrumental analytical methods was summarized in a 2009 review [20].

Periodate salts have found practical application as environmentally friendly oxidizers in pyrotechnic formulations [21]. Moretti, Sabatini, and Chen have developed the periodate based pyrotechnic propellants that perform similarly to perchlorates but are not toxic [21]. The mixtures of periodate salts with magnalium (1:1 alloy magnesium-aluminum) produce a bright flash of light.

Iodine pentafluoride (IF_5) is the most thermodynamically stable fluoride among the fluorides of chlorine, bromine, and iodine. It is manufactured in the USA on a scale of several hundred tons per year for applications as an industrial fluorinating reagent. It is commercially available as a liquid in steel cylinders up to 1350 kg capacity [16]. Iodine pentafluoride is a relatively safe compound that can be handled in glass equipment. One of the important areas of practical application of iodine pentafluoride is the production process for volatile uranium hexafluoride in nuclear power engineering [22]. Iodine pentafluoride has found some application for the preparation of graphite fluorides, which are used as cathode materials in lithium batteries [23] and also as lubricants [24].

3. Results and Discussion

Common hypervalent iodine reagents are occasionally used in chemical industry as the reagents for production of important pharmaceutical intermediates. Zanka and coworkers have developed a process

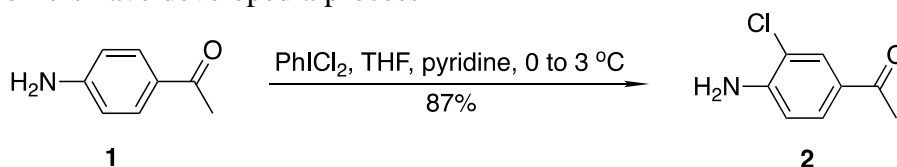


Fig. 1. Industrial application of (dichloroiodo)benzene

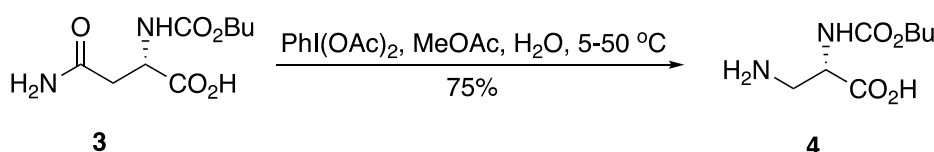


Fig. 2. Large-scale synthesis of N-protected α -amino-L-alanine derivatives

A nonexplosive formulation of important hypervalent iodine oxidant, SIBX, consisting of 2-iodoxybenzoic acid, benzoic acid, and isophthalic acid, has been developed by Quideau and coworkers [28]. SIBX is available as a reagent for industrial applications in bulk quantities. SIBX has similar to 2-iodoxybenzoic acid (IBX) reactivity in the reactions of hydroxylative phenol dearomatization [29], oxidation of sulfides

for the large scale (20–25 kg) preparation of (dichloroiodo)benzene (PhICl_2) by the reaction of iodo-benzene with chlorine at -3 to $+4$ °C in dichloromethane [25]. Special emphasis was given in this work to the development of a safe procedure for the large scale handling of PhICl_2 which, according to the differential thermal analysis (DTA) studies, can decompose exothermically at about 100 °C. (Dichloroiodo)benzene was further used as a reagent for production of 4-amino-3-chloroacetophenone (**2**), which is a common intermediate to many of the COX-II (cyclooxygenase-2) selective inhibitors. The chlorination of aminoacetophenone (**1**) with PhICl_2 was carried out in THF in the presence of pyridine at about 0 °C to selectively produce product **1** in good yield (Fig. 1). This process was successfully scaled up in a pilot plant to produce up to 25 kg of product **2** with 94% purity [25].

(Diacetoxyiodo)benzene is a preferred reagent for performing Hofmann rearrangement in large scale. A comparative study of various oxidants (hypochlorite, hypobromide, N-bromosuccinimide, etc.) has demonstrated that $\text{PhI}(\text{OAc})_2$ is the best reagent for the synthesis of N-protected α -amino-L-alanine derivatives from N-protected asparagines [26]. In particular, the optically pure $N\alpha$ -n-Boc-L- α,β -diaminopropionic acid **4** ($R = \text{CO}_2\text{Bu}$) was prepared by treatment of N-Boc-protected asparagine **3** with (diacetoxyiodo)benzene in 15–20 kilogram quantities (Fig. 2) [27].

into sulfoxides [30], oxidative demethylation of phenolic methyl aryl ethers [28], and many other useful oxidative transformations.

4. Applications of hypervalent iodine compounds as polymerization promoters

Diaryliodonium salts have found industrial application as photoinitiators for cationic photopolymerizations [31–33]. Photoinitiated cationic polymeriza-

tion is of great practical interest due to its applicability for the curing of coatings and printing inks [32], and for photoresist technology used in lithography [33]. General synthetic methods, properties, and photochemistry of diaryliodonium salts as photoinitiators were reviewed by Crivello in 1984 [34]. Several aspects of applications of hypervalent iodine compounds in polymer science were discussed in a recently published book chapter [9].

Crivello and coworkers have first reported that iodonium salts having BF_4^- , PF_6^- , AsF_6^- , or SbF_6^- counter ions can be used as efficient photoinitiators for the cationic polymerization of various monomers [35]. The mechanism of iodonium salt photolysis involves radical-cations and aryl radicals as key intermediates (Fig. 3). The photoexcited iodonium salt **5** decomposes to produce iodonium radical-cation **6**, aryl radical **7**, and anion **8** [35]. This is a highly efficient process because of the very low bond energy of the C–I bond (26–27 kcal/mol). Reaction of the iodonium radical-cation **6** with the solvent (S–H) produces a protonated aryliodonium cation **9** and a radical $\text{S}\cdot$ derived from the solvent. The aryliodonium cation **9** immediately deprotonates producing the corresponding Brønsted acids HX ($\text{X} = \text{BF}_4$, PF_6 , AsF_6 , or SbF_6). These acids act as the real initiators of cationic polymerization when diaryliodonium salts are employed in the cationic photopolymerization of appropriate monomers. According to this mechanism, diaryliodonium salts are classified of photoacid generators (PAGs), which find broad applications in the manufacturing of protective coatings, smart cards, 3D rapid prototyping, UV adhesives, semiconductor devices, anti-reflective coatings, holograms, etc.

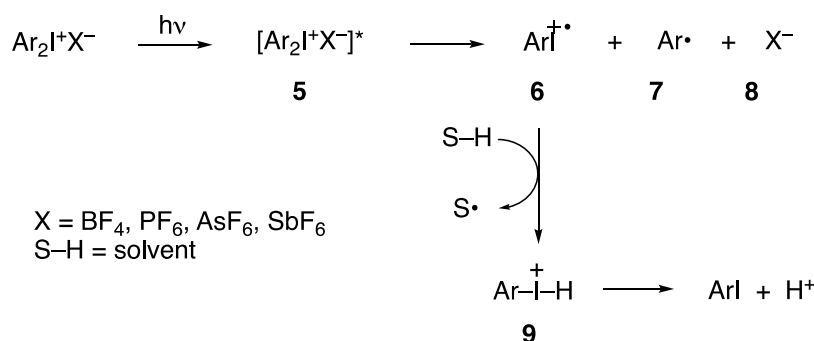


Fig. 3. The mechanism of iodonium salt photolysis

In the groundbreaking paper [35], Crivello and coworkers have found that the nature of the anion (X) does not have any significant effect on the photosensitivity of the iodonium salt. In fact, the photolysis rates of diaryliodonium salts having the same cations Ar_2X^+ but different nonnucleophilic counter ions (BF_4^- , PF_6^- , AsF_6^- , or SbF_6^-) are identical. The structure of the cation Ar_2X^+ also has little effect on the photodecomposition of diaryliodonium salts. Iodonium salts can be used as photoinitiators in various cationic polymerizations utilizing alkenes, epoxides, cyclic ethers, lactones, and cyclic sulfides as the monomers.

Iodonium salts have been used as photoinitiators in the following polymerization studies: copolymerization of butyl vinyl ether and methyl methacrylate by combination of radical and radical promoted cationic mechanisms [36], thermal and photopolymerization of divinyl ethers [37], photopolymerization of vinyl ether networks using an iodonium initiator [38], dual photo- and thermally initiated cationic polymerization of epoxy monomers [39], preparation and

properties of elastomers based on a cycloaliphatic diepoxide and poly(tetrahydrofuran) [40], photo-induced crosslinking of divinyl ethers [41], cationic photopolymerization of 1,2-epoxy-6-(9-carbazolyl)-4-oxahexane [42], preparation of interpenetrating polymer network hydrogels based on 2-hydroxyethyl methacrylate and N-vinyl-2-pyrrolidone [43], photopolymerization of unsaturated cyclic ethers [44], and numerous other works.

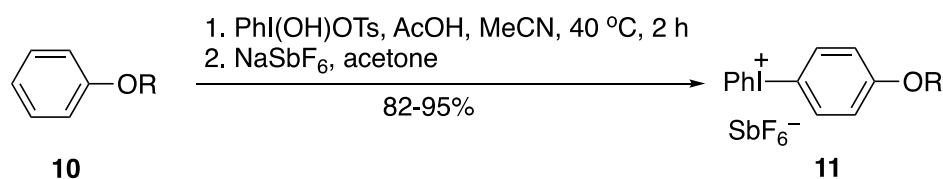
Several different initiation methods have been used in the studies of polymerizations promoted by iodonium salts including the following: visible laser irradiation [45], dual photo- and thermally initiated cationic polymerization [37], and two-photon photopolymerization initiation system [46]. In particular, a dual photo- and thermal initiation system utilizing the selective inhibition of photoinitiated cationic polymerization of epoxides by dialkyl sulfides has been developed [39]. This dual system consisting of iodonium salt/dialkyl sulfide can be activated by UV irradiation in the presence of a monomer and then subsequently be polymerized by the application of

heat. The presence of dialkyl sulfides causes termination of the initial polyether chains at an early stage due to the formation of stable trialkylsulfonium salts. Such an activated system is dormant at room temperature; however, the sulfonium salts are capable of reinitiating ring-opening polymerization upon heating. The dual photo- and thermal cure systems have potential applications in adhesives, potting resins, and composites [39]. A different type of initiation system based on the two-photon photopolymerization initiation, consists of a photosensitizer dye and the photoinitiator diaryliodonium salt encapsulated by methylated- β -cyclodextrin [46]. This system can be used as an effective photoinitiator for two-photon photopolymerization in aqueous solution.

Numerous studies have been devoted to the development of the more efficient photoinitiators based on modified iodonium salts. In contrast to the original observations of Crivello that the structure of iodonium salt does not affect its photodecomposition [35], it has been demonstrated in the later works that both anionic and cationic part of iodonium salts may play an important role in the effectiveness of the photoinitiator. A detailed study on the participation of the anion and alkyl substituent of diaryliodonium salts in photoinitiated cationic polymerization reaction of epoxides was published by Park and coworkers [47]. In particular, it was found that alkyl substituted diphenyliodonium cations, (e.g. bis(4-tert-butyl-phenyl)iodonium and 4-cumenyl-4'-tolyliodonium salts) have

higher photoacid generation efficiency compared to the unsubstituted diphenyliodonium salts. The low nucleophilicity and large size of the anions increase the rate of polymerization, with $\text{PF}_6^- < \text{AsF}_6^- < \text{B}(\text{C}_6\text{F}_5)_4^-$ general order of reactivity [47]. The larger anions are more loosely bound to the end of the growing cationic chain resulting in increased electrophilicity of cationic centers and faster polymerization. The $\text{B}(\text{C}_6\text{F}_5)_4^-$ is the largest anion in this series and the most loosely bound, while PF_6^- is the smallest and, therefore, the most tightly bound anion. For comparison, in the case of the most nucleophilic triflate anion (CF_3SO_3^-), cationic polymerization of epoxides was not observed [47].

The synthesis and characterization of a series of (4-alkoxyphenyl)phenyliodonium salts **11**, which are excellent photo- and thermal initiators for the cationic polymerization of vinyl and heterocyclic monomers, has been reported by Crivello and Lee [31]. Iodonium salts **11** can be prepared by the reaction of alkoxybenzenes **10** with [hydroxy(tosyloxy)iodo]-benzene followed by the anion exchange with sodium hexafluoroantimonate (Fig. 4). Products **11** have excellent solubility and photoresponse characteristics, which make them especially attractive for use in UV curing applications. Moreover, iodonium salts **11** with alkoxy chains of eight carbons and longer are essentially nontoxic, compared to Ph_2ISbF_6 , which has an oral LD_{50} of 40 mg/kg (rats) [31].



R = Me, C_8H_{17} , $\text{C}_{10}\text{H}_{21}$, $\text{C}_{11}\text{H}_{23}$, $\text{C}_{14}\text{H}_{29}$, $\text{C}_{15}\text{H}_{31}$, $\text{C}_{16}\text{H}_{33}$, $\text{C}_{18}\text{H}_{37}$

Fig. 4. Synthesis of (4-alkoxyphenyl)phenyliodonium salts

Shirai, Kubo, and Takahashi have synthesized and tested as cationic photoinitiators several new alkyl substituted diaryliodonium **12-17** (Fig. 5) possessing high solubility and low toxicity [48]. In combination with 2-ethyl-9,10-dimethoxyanthracene as the photosensitizer, these alkyl substituted iodonium salts have demonstrated an especially high photocuring ability.

Hartwig and coworkers reported the preparation and properties of (9-oxo-9H-fluoren-2-yl)-phenyliodonium hexafluoroantimonate **19**, which is useful as a photoinitiator for the cationic polymerization of epoxides [49]. Iodonium salt **19** was prepared by the

reaction of (diacetoxyiodo)benzene with fluorenone (**18**) followed by anion exchange with sodium hexafluoroantimonate (Fig 6). Compound **19** is a more effective photoinitiator compared to the conventional iodonium salts and has the advantage of intramolecular photosensitization.

Alkynyl(phenyl)iodonium salts have also been tested for application as cationic photoinitiators [50]. In particular, the high activity of phenyl(phenylethynyl)iodonium hexafluorophosphate as a photoinitiator has been established by photo-DSC exper-

iments in direct irradiation and in photosensitized initiation using 9,10-dibutylanthracene, 2-isopropylthioxanthone, and benzophenone as sensitizers.

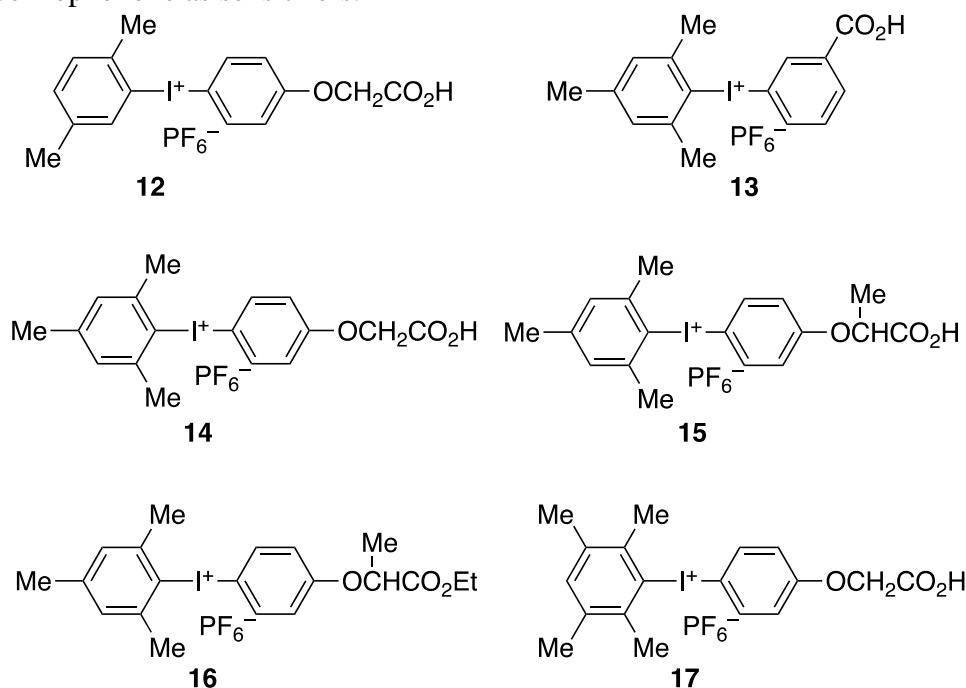


Fig. 5. Alkyl substituted diaryliodonium hexafluorophosphates: efficient photoinitiators with high solubility and low toxicity

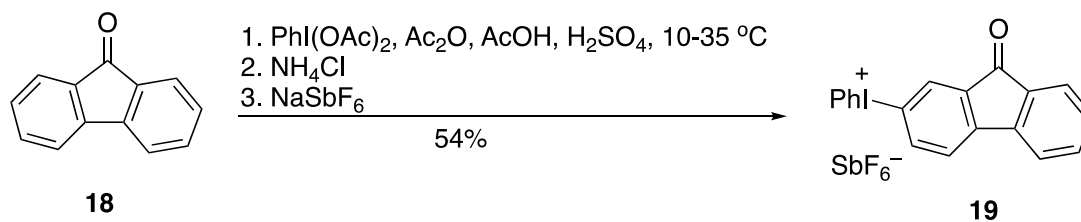


Fig. 6. Preparation of (9-oxo-9H-fluoren-2-yl)-phenyliodonium hexafluoroantimonate

Diaryliodonium butyltriphenylborate salts **20-23** (Fig. 7) were prepared by the anion exchange of respective diaryliodonium halides with tetramethylammonium butyltriphenylborate and evaluated as photoinitiators for the polymerization of acrylates⁴⁹. Butyltriphenylborate salts **20-23** were found to be more efficient photoinitiators than the corresponding tetraphenylborate salts, Ar₂IBPh₄. A study of the photoreaction of iodonium borate salts with a model monomer, methyl methacrylate, has demonstrated that irradiation of iodonium salts **20-23** simultaneously generates a butyl radical from the borate anion and an aryl radical from the iodonium cation. Both butyl and aryl radicals initiate polymerization. In contrast, iodonium tetraphenylborate salts, Ar₂IBPh₄, release only aryl radical from the iodonium cation. Overall, iodonium butyltriphenyl borate salts **20-23** are efficient photoinitiators even when used with visible light [51].

Georgiev, Spyroudis, and Varvoglis have originally reported that [bis(acyloxy)iodo]arenes can be used as effective photoinitiators of cationic and radical polymerization [52]. Under photochemical conditions, (diacetoxyiodo)benzene and [bis(trifluoroacetoxy)iodo]benzene are efficient initiators for the homopolymerizations of 2-(dimethylaminoethyl) methacrylate (DMAEM) and methyl methacrylate (MMA) and also for the copolymerizations of DMAEM with MMA or styrene [53]. The mechanism of the photoinitiation involves initial homolytic decomposition of (diacetoxyiodo)benzene (**24**), producing acetyl **26** and iodanyl **25** radicals (Fig 8) [54, 55]. The actual initiators of radical polymerization are methyl radicals **27** generated by the decarboxylation of acetyl radical **26**, as proved by the radical scavenger method [56]. The iodanyl radical **25** can further undergo both homolytic and heterolytic decomposition; homolytic fragmentation produces additional acetyl and methyl radicals, while the heterolytic fragmentation of

iodanyl radical **25** generates iodobenzene cation-radical **23**, which acts as the initiator of cationic polymerization [54].

The photoiniferter ability of [bis(acyloxy)iodo]arenes during the bulk polymerization of methyl methacrylate, styrene and N-vinylpyrrolidone has been reported by Georgiev [54]. Photoiniferter is a chemical compound that has a combined function of being a radical initiator, transfer agent, and terminator in a photolytically induced polymerization [57]. Under visible light [bis(acyloxy)iodo]arenes initiate the

"pseudoliving" radical polymerization, while a conventional radical or cationic polymerizations are initiated by the iodane decomposition under UV irradiation. It was suggested that the spectral selectivity of the decomposition of iodanyl radical **25** (Fig. 8) and the relative instability of the ends of the iodane macromolecule are the reasons of photoiniferter ability of [bis(acyloxy)iodo]arenes [54].

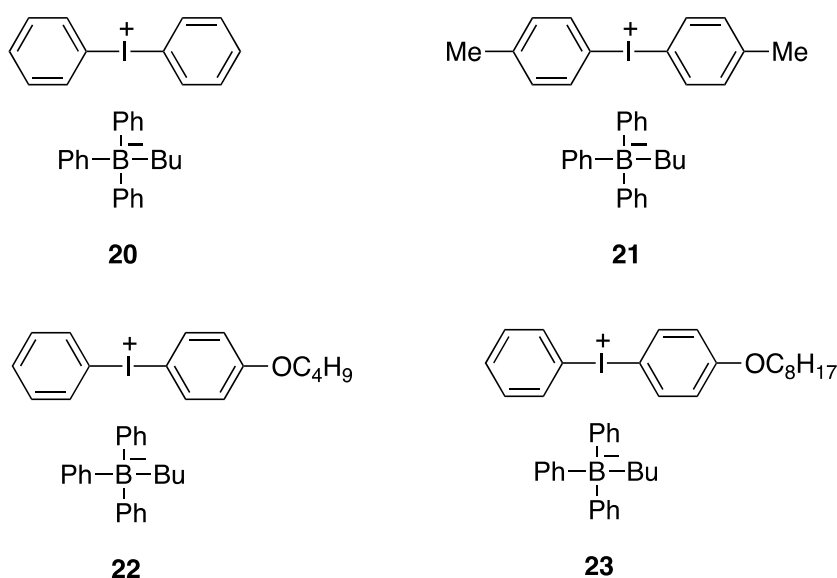


Fig. 7. Photoinitiators based on diaryliodonium butyltriphenylborate salts

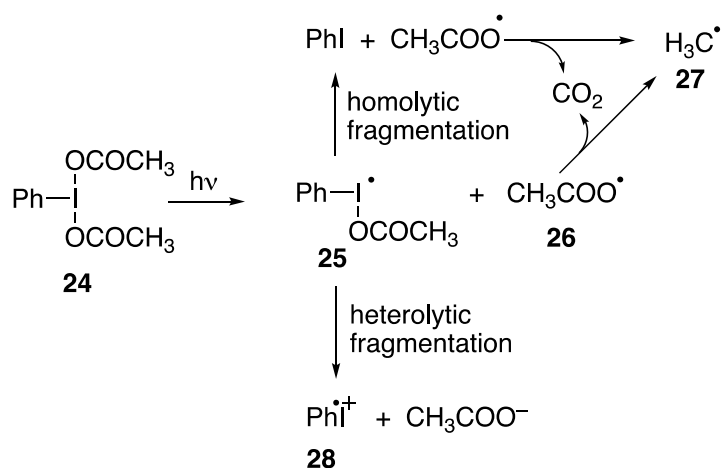


Fig. 8. The mechanism of photolysis of (diacetoxyiodo)benzene

The acetoxy groups in PhI(OAc)_2 can be exchanged with methacrylic acid in various solvents yielding [acetoxy(methacryloyloxy)iodo]benzene or (dimethacryloyloxyiodo)benzene. These two [bis(acyloxy)iodo]arenes can serve as inimers due to the presence of polymerizable moiety and the easy generation of radicals upon thermal or light-induced

homolysis of the I–O bonds [58]. After adding (diacetoxyiodo)benzene to the mixtures of methacrylic acid and methyl methacrylate and heating to 80 °C, the branched or transiently crosslinked polymers are formed. In contrast, when homopolymerization of methyl methacrylate is initiated by PhI(OAc)_2 in the absence of methacrylic acid, no branching or gelation is observed [58].

Tsarevsky has reported that hypervalent iodine compounds can be used for direct azidation of polystyrene and consecutive click-type functionalization [59]. Polystyrene can be directly azidated in 1,2-dichloroethane or chlorobenzene using a combination of trimethylsilyl azide and (diacetoxyiodo)benzene. The 2D NMR HMBC spectra indicate that the azido groups are attached to the polymer backbone and also possibly to the aryl pendant groups. Approximately one in every 11 styrene units can be modified by using a ratio of $\text{PhI}(\text{OAc})_2$ to trimethylsilyl azide to styrene units of 1 : 2.1 : 1 at 0 °C for 4 hours followed by heating to 50 °C for 2 hours in chlorobenzene. The azidated polymers can be further used as backbone precursors in the synthesis of polymeric brushes with hydrophilic side chains via a copper-catalyzed click reaction with poly(ethyleneoxide)-monomethyl ether 4-pentynoate [59].

Han and Tsarevsky have developed a method for the preparation of the azido-substituted linear and branched polymers using the $\text{PhI}(\text{OAc})_2/\text{NaN}_3$ initiating system [60]. This method takes advantage of the efficient exchange of the acetoxy groups in $\text{PhI}(\text{OAc})_2$ with azide generating hypervalent iodine azides $\text{PhI}(\text{N}_3)(\text{OAc})$ and $\text{PhI}(\text{N}_3)_2$. Hypervalent iodine azides rapidly decompose at ambient temperature producing iodobenzene and azide radicals, which initiate the polymerization of methyl methacrylate at forming polymers with the azide group at the α -terminus. The termination by coupling of the propagating radicals with azide radicals leads to the formation of low-molecular weight linear polymers with an azide group at the ω -end. When the polymerization is carried out in the presence of divinyl compounds as crosslinkers, the highly branched polymers are produced. Overall, this sequence of reactions provides an efficient route to mono- and diazide-capped linear or multi-azidated branched polymers that can be further functionalized via click coupling reactions with alkynes, such as propargyl 4-(1-pyrenyl)butyrate [60].

5. Iodonium compounds as reagents for nucleophilic fluorination in Positron Emission Tomography (PET)

In recent years, reactions of arylodonium compounds with fluoride anion have found important practical application in Positron Emission Tomography (PET) as a fast and convenient method for the introduction of the radioactive $[^{18}\text{F}]$ -fluoride into radiotracer molecules [10, 61-63]. PET is a powerful method of molecular imaging based on the use of radiopharmaceuticals labeled with the short-lived positron-emitting radioisotopes ^{11}C , ^{18}F , ^{15}O , and ^{13}N . Fluorine-18 is the most commonly used in PET radioisotope owing of its a short positron linear range in tissue (2.3 mm) which gives the highest resolution PET images of all the available positron emitters. $[^{18}\text{F}]$ -isotope has a convenient half-life of 109.7 min, which allows sufficient time for multistep synthetic labeling reactions. $[^{18}\text{F}]$ -isotope is produced with a cyclotron, either as molecular fluorine gas or as a particularly useful $[^{18}\text{F}]$ -fluoride anion. $[^{18}\text{F}]$ -fluoride is generally used for the fluorination of electron-deficient arenes via aromatic nucleophilic substitution reaction. Nucleophilic $[^{18}\text{F}]$ -anion is produced by the nuclear reaction from $[^{18}\text{O}]$ -water. The obtained aqueous $[^{18}\text{F}]$ -fluoride is a poor nucleophile because of its solvation. The addition of the phase-transfer reagent Kryptofix-222 is usually required to improve the reactivity of the $[^{18}\text{F}]$ fluoride ion in nucleophilic substitution reactions.

5.1. Aryliodonium salts as PET precursors

Reactions of diaryliodonium salts with the cyclotron-produced $[^{18}\text{F}]$ -potassium fluoride in the presence of a phase-transfer reagent Kryptofix-222 (K222) provide a fast and convenient method of $[^{18}\text{F}]$ -fluorination as outlined in Fig. 9. The high reactivity of arylodonium salts Ar_2IX in these reactions is explained by the "hyperleaving group ability" of the ArI group; for example, the leaving group ability of PhI is about million times greater than the triflate group [64].

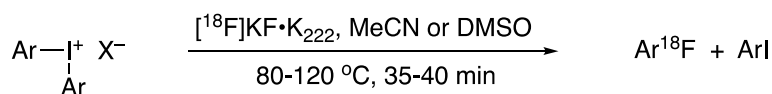
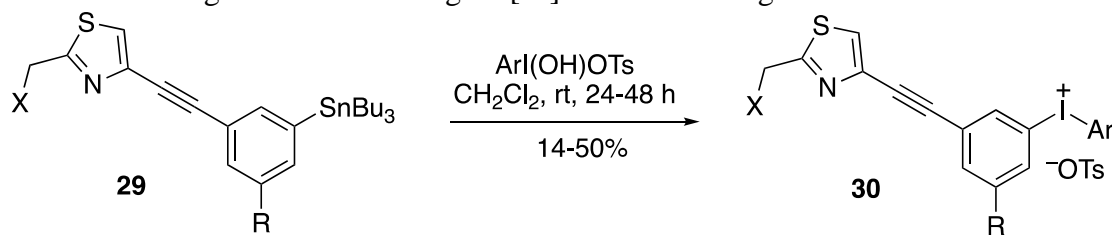


Fig. 9. General scheme of nucleophilic $[^{18}\text{F}]$ -fluorination with iodonium salts

Diaryliodonium salts represent one of the most stable and well-investigated class of organoidodine(III) compounds. A summary of synthetic approaches to iodonium

salts and their reactivity was provided in our previous review [65]. The most common methods of preparing iodonium PET precursors are based on a mild reaction of

arylstannanes (ArSnBu_3) with [hydroxy(tosyloxy)iodo]arenes [$\text{ArI}(\text{OH})\text{OTs}$]. A specific example of the application of this approach to the preparation of iodonium precursors **30** from stannane **29** in the synthesis of mGluR5 PET radioligands is shown in Fig. 10 [66].



X = H or F; R = H or CN; Ar = Ph or 4-MeOC₆H₄

Fig. 10. Synthesis of PET iodonium precursors for mGluR5 PET radioligands

Analogous procedure can be used for the preparation of heteroaryliodonium salts. For example, iodonium salts **32** were prepared by reaction of stannylarenes **31** with the respective $\text{ArI}(\text{OH})\text{OTs}$ (Fig. 11). Heteroaryliodonium tosylates **32** were used as precursors in synthesis of important PET radioligands for β -amyloid plaques [67].

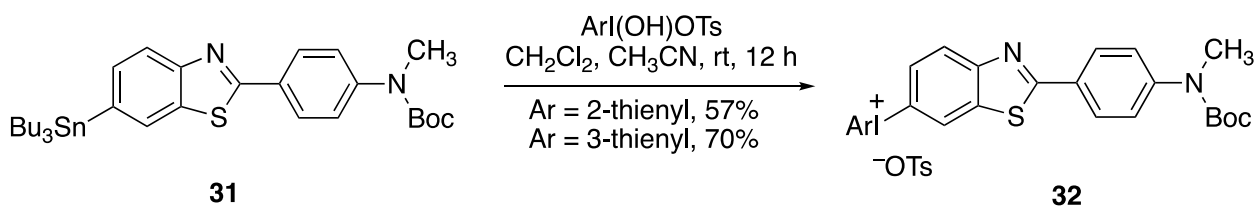
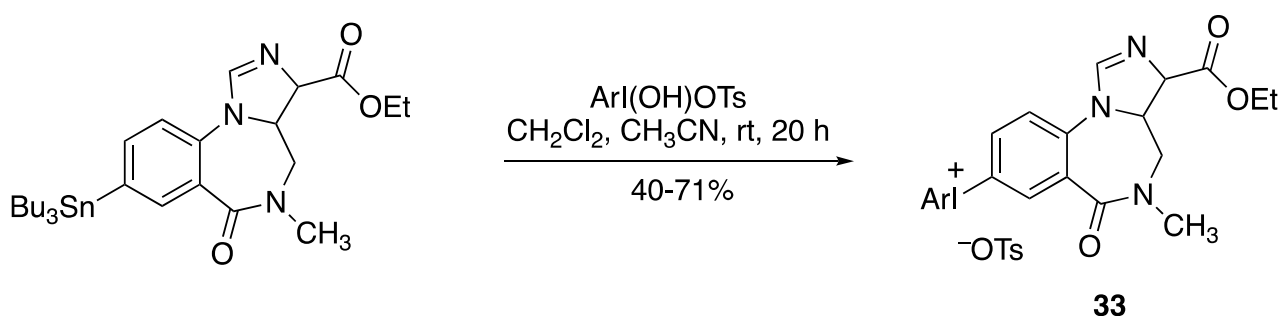


Fig. 11. Preparation of heteroaryliodonium PET precursors **32**



Ar = 2-thienyl, 3-thienyl, Ph, 4-MeOC₆H₄, 3-MeOC₆H₄, 4-MeC₆H₄

Fig. 12. Preparation of PET precursors to radiosynthesis of [19F]flumazenil

The regioselectivity of nucleophilic [18F]-fluorination is controlled by electronic factors and, most important, by the bulk of the ortho-substituents on the rings. In particular, the presence of a bulky ortho-substituent changes the regioselectivity allowing fluorination of the electron-rich ortho-substituted ring. For ex-

ample, the reaction of 2,4,6-trimethylphenyl(phenyl)iodonium triflate **34** with [18F]-fluoride selectively forms fluoroarene **35** along with iodobenzene as a byproduct (Fig. 13) [69]. However, the presence of a copper catalyst, can reverse the regioselectivity of nucleophilic fluorination [70].

A similar procedure was employed in the synthesis of aryl- and thienyl derived iodonium tosylates **33** (Fig 12). Reaction of PET precursors **33** with [18F]-fluoride was applied in the radiosynthesis of [18F]flumazenil, an important radiopharmaceutical for evaluation of the central benzodiazepine receptor (cBZR) concentration in brain [68].

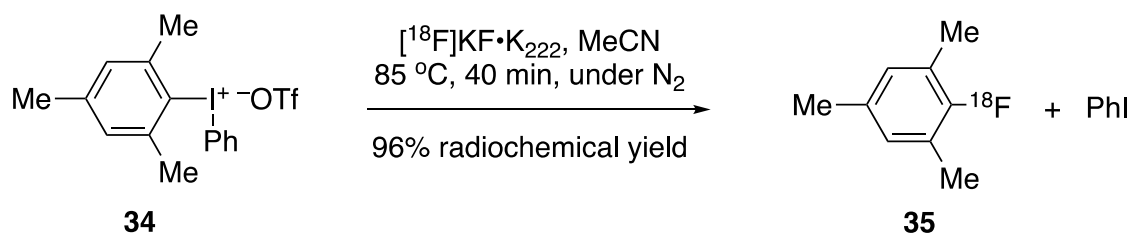


Fig. 13. Effect of ortho-substituent on the regioselectivity of radiofluorination

Several examples of preparation of PET radioligands are discussed below. Zhang and coauthors have reported the synthesis of a PET ligand [^{18}F]DAA1106 **37** by reaction of arylidonium tosylate **36** with [^{18}F]-fluoride anion (Fig. 14) [71]. Compound **37** is used as a PET ligand for imaging a peripheral-type benzodiazepine receptor.

Katzenellenbogen and coauthors have reported the synthesis and evaluation of two ^{18}F -labeled analogues of important PPAR γ agonist farglitazar [72].

The radioligand **39** was obtained by nucleophilic fluorination of idonium tosylate **38** in good radiochemical yield (Fig. 15).

Pike and coauthors developed synthetic approach to 3-fluoro-1-[(thiazol-4-yl)ethynyl]arenes **40** by radiofluorination of arylidonium tosylates **30** (Fig. 16) [66]. Compounds **40** belong to an important class of high-affinity metabotropic glutamate subtype 5 receptor (mGluR5) ligands and are used as radioligands for molecular imaging of brain mGluR5 in humans.

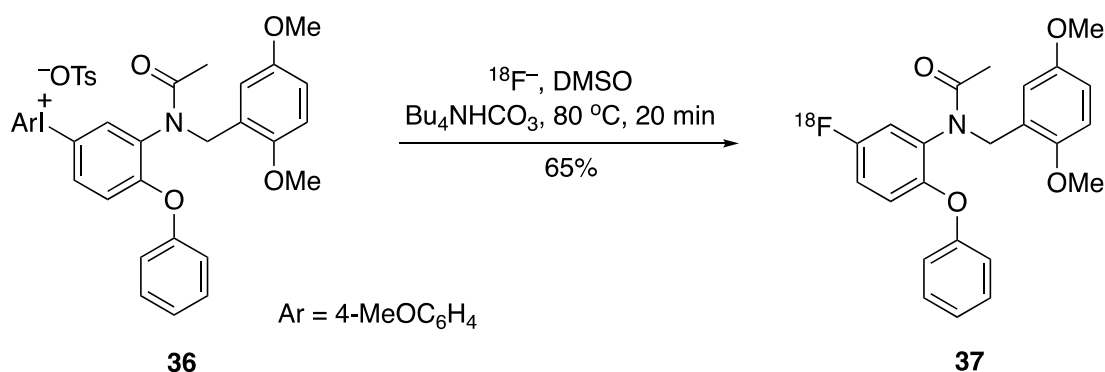


Fig. 14. Synthesis of PET ligand [^{18}F]DAA1106

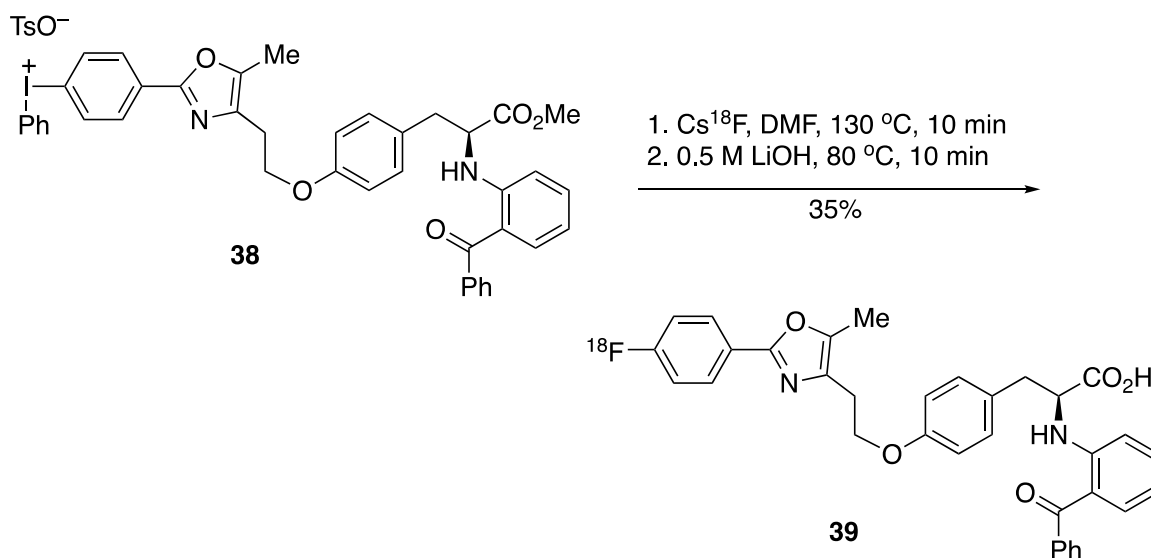
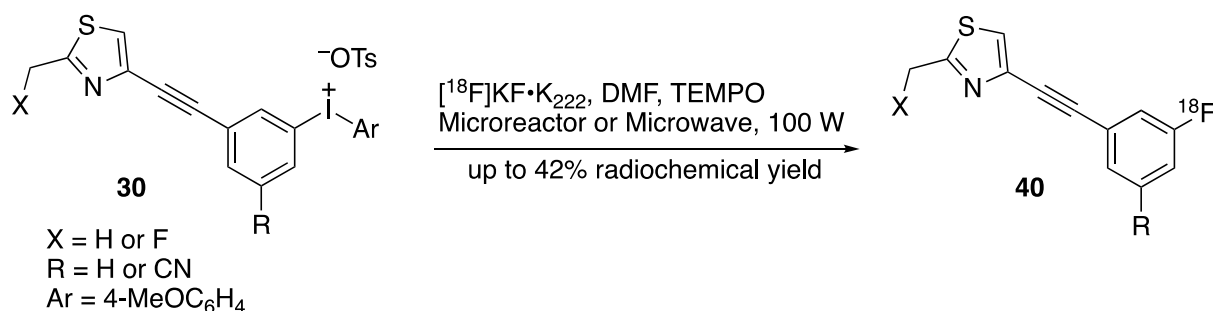


Fig. 15. Synthesis of the ^{18}F -labeled analogue of PPAR γ agonist farglitazar

Fig. 16. Preparation of radioligands **41**

5.2. Aryliodonium ylides as PET precursors

The use of iodonium ylides as PET precursors for labeling reactions with fluorine-18 has recently been reviewed [62]. In contrast to the reactions of aryliodonium salts, the reactions of the iodonium ylides are completely regioselective. Even electron-rich labeled fluoroarenes can be selectively prepared using aryl iodonium ylides and $[^{18}\text{F}]$ -fluoride anion.

Aryliodonium ylides ArICR_2 with electron-withdrawing substituent R (usually, carbonyl or sulfonyl group), represent an important class of iodonium compounds bearing a carbanionic carbon atom. [73]. Owing to the charge distribution, the attack of external nucleophiles is exclusively directed toward the aromatic ring, which makes aryliodonium ylides especially attractive as PET labeling precursors.

The most practically important iodonium ylides, the dicarbonyl derivatives $\text{PhIC}(\text{COR})_2$, are prepared

by a reaction of (diacetoxyiodo)benzene with the appropriate dicarbonyl compound under basic conditions. A general procedure for the synthesis of phenyliodonium ylides **42** from malonate esters **41** is based on the treatment of esters **41** with (diacetoxyiodo)benzene in dichloromethane in the presence of potassium hydroxide (Fig. 17) [74]. Iodonium ylides **42** have low stability at room temperature and should be stored in a refrigerator.

Cardinale and Ermert have developed a simplified procedure for the synthesis of aryliodonium ylides directly from the respective aryliodides [75]. In this method, ylides **44** are synthesized by a one-pot procedure shown in Fig. 18. Iodoarenes **43** are initially oxidized with *m*CPBA and then the suspension of Meldrum's acid and potassium hydroxide is added to produce ylides **44**.

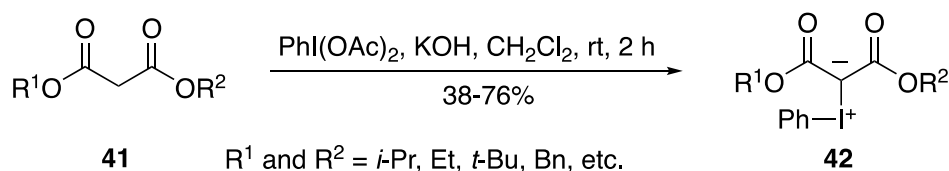
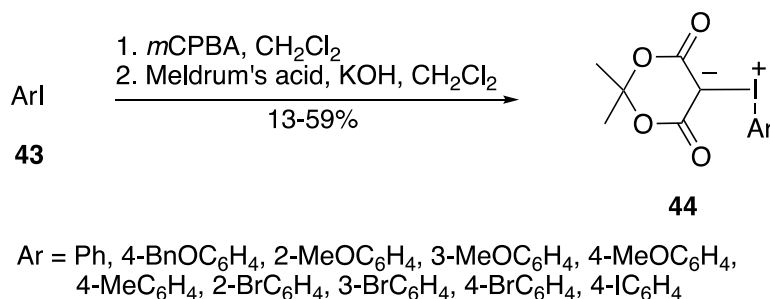


Fig. 17. Preparation of iodonium ylides



*m*CPBA = *m*-chloroperoxybenzoic acid

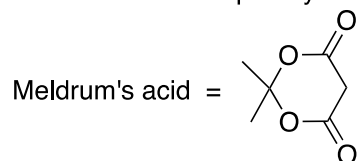
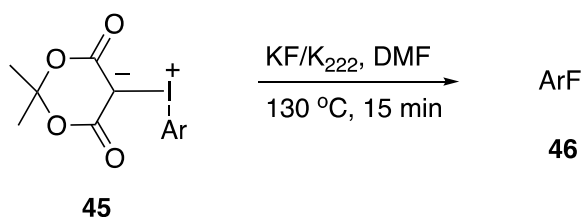


Fig. 18. One-pot procedure for the synthesis of iodonium ylides from iodoarenes

Satyamurthy and Barrio have first reported that reactions of ylides with nucleophiles in polar aprotic solvents such as dimethylsulfoxide, acetonitrile, tetrahydrofuran, and dimethylformamide result in regioselective substitution of the nucleophile on the aromatic ring [76]. In particular, heating phenyliodonium ylides **45** with dried KF-Kryptofix (K222) complex in DMF forms fluoroarenes **46** as the main product (Fig. 19).



Ar = Ph, 4-MeC₆H₄, 2,4,6-Me₃C₆H₂, 2-MeOC₆H₄, 3-MeOC₆H₄, 4-MeOC₆H₄, 4-BrC₆H₄

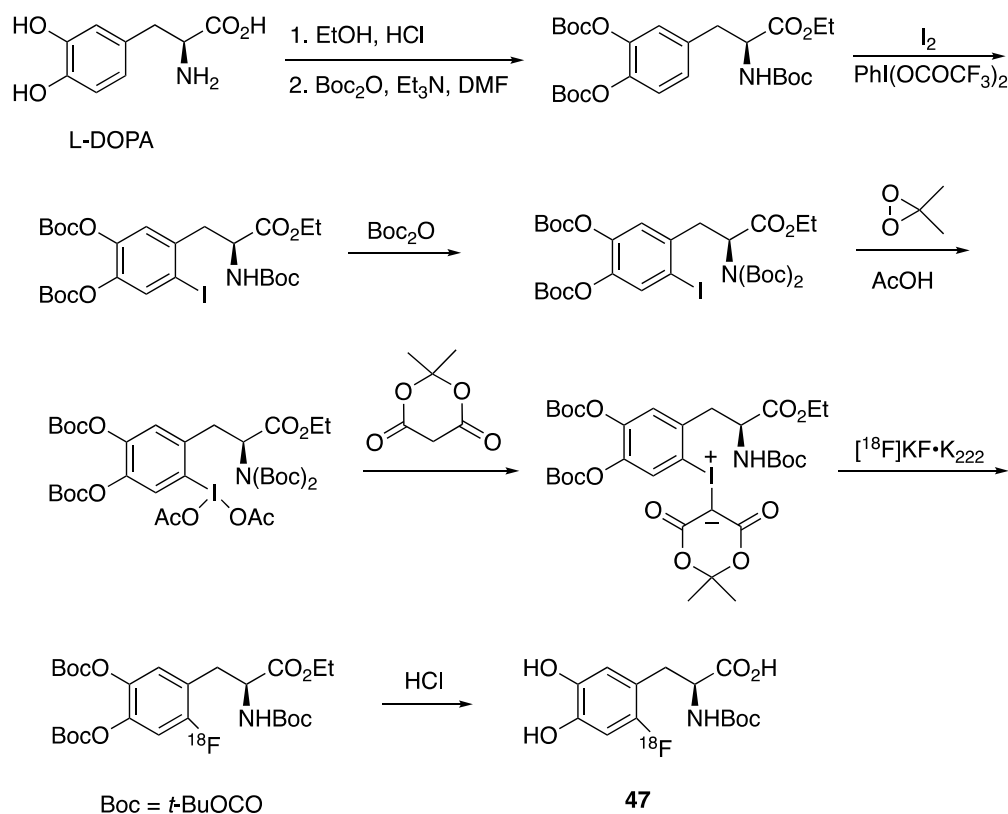


Fig. 20. Radiosynthesis of L-6-[¹⁸F]fluoroDOPA

Vasdev, Liang, and co-workers have demonstrated that the spirocyclic aryliodonium ylides can serve as versatile precursors for efficient radiolabelling of a diverse range of non-activated (hetero)arenes, highly functionalized small molecules, building blocks, and radiopharmaceuticals [77, 78]. For example, the reac-

Fig. 19. Nucleophilic fluorination of iodonium ylides

This approach has been employed for the radio-fluorination of protected L-DOPA derivatives [76]. A radiochemically pure amino acid L-6-[¹⁸F]fluoroDOPA **47** has been produced in the amounts usable for human PET studies as shown in Fig. 20. The fluorine-18 labeled L-DOPA is a useful PET imaging agent for mapping dopamine related brain disorders and is the PET biomarker of choice for the diagnosis of Parkinson's disease.

tions of ylides **48** and **50** under continuous-flow microfluidic condition offers automated synthetic procedure for the preparation of a radiopharmaceutical, 3-[¹⁸F]fluoro-5-[(pyridin-3-yl)ethynyl]benzonitrile ([¹⁸F]FPEB) **49**, and a routinely used building block for click-radiochemistry, 4-[¹⁸F]fluorobenzyl azide **51** in high radiochemical conversion (RCC) (Fig. 21).

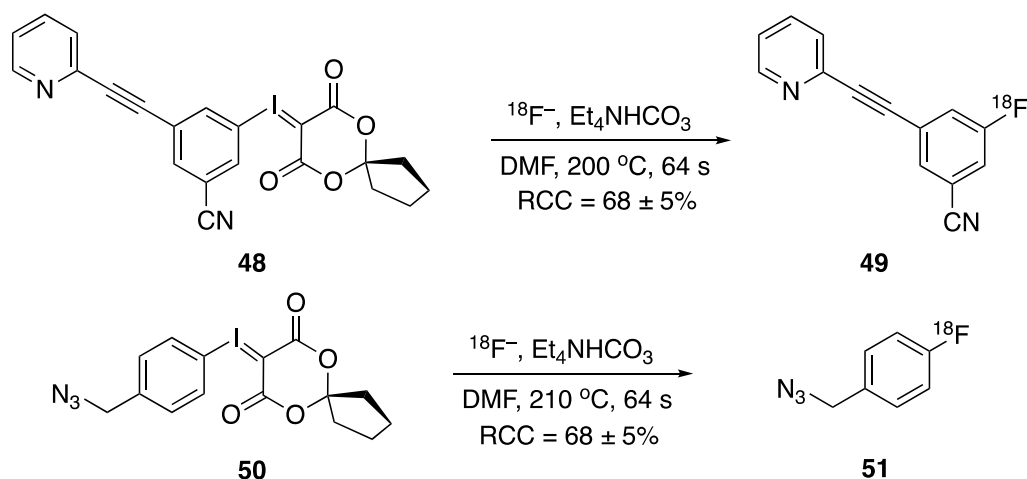


Fig. 21. Nucleophilic radiofluorination of spirocyclic arylidonium ylides

6. Conclusion

Summarized in this review publications demonstrate a great potential of hypervalent iodine compounds as polymerization initiators and promoters of various types. In particular, diaryliodonium salts are useful industrial photoinitiators for cationic photopolymerizations. [Bis(acyloxy)iodo]arenes can be used as efficient initiators for radical polymerization of alkenes. Hypervalent iodine compounds have also found many biomedical uses. Especially important

are the applications of arylidonium salts and ylides as precursors to [^{18}F]-fluorinated radiotracers for Positron Emission Tomography. Various hypervalent iodine compounds can also serve as valuable reagents for pharmaceutical industry.

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