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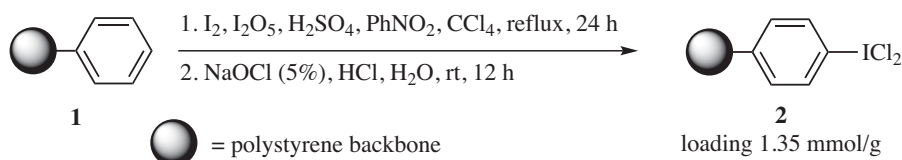
Recyclable Hypervalent Iodine Reagents

Despite their useful reactivity and environmentally benign nature, common hypervalent iodine reagents derived from iodobenzene or simple aryl iodides are not perfect with respect to the principles of green chemistry. According to one of the basic principles of green chemistry, recyclable reagents are superior to stoichiometric reagents [1]. The most widely used hypervalent iodine(III) reagents, such as (dichloroiodo)benzene, (diacetoxyiodo)benzene, iodosylbenzene and [hydroxy(tosyloxy)iodo]benzene, are based on the oxidized form of iodobenzene and the reactions of these reagents with organic substrates produce stoichiometric amount of iodobenzene as a waste product, which results in low atom economy and complicated isolation and purification of the products. Likewise, the most common hypervalent iodine(V) reagents, IBX and DMP (Section 3.2), produce 2-iodobenzoic acid as a waste by-product. Polymer-supported hypervalent iodine reagents, as well as recyclable nonpolymeric reagents, overcome these drawbacks and in general have the same reactivity as their monomeric analogues. Moreover, polymer-supported reagents have found broad application in solid-phase and combinatorial high-throughput synthesis techniques. Attachment of a chemical reagent to an insoluble polymer matrix enables easy reaction work up by simple filtration, automated parallel synthesis and fast reaction optimization [2–4]. Numerous polymer-supported hypervalent iodine(III) and iodine(V) reagents have been developed since the beginning of the twenty-first century. Several reviews on polymer-supported, as well as nonpolymeric recyclable hypervalent iodine reagents, have been published [5–9].

5.1 Polymer-Supported Iodine(III) Reagents

The first polymer-supported hypervalent iodine reagent, poly[(dichloroiodo)styrene], was prepared by chlorination of iodinated polystyrene in the early 1980s [8]. This method, however, involves the initial preparation of iodinated polystyrene under harsh conditions (160 h, 110 °C), requires the use of hazardous chlorine gas and affords poly[(dichloroiodo)styrene] with a relatively low loading of active chlorine. An optimized one-pot preparation of polystyrene-supported (dichloroiodo)benzene **2** (loading of $-\text{ICl}_2$ up to 1.35 mmol g⁻¹) from polystyrene **1**, iodine and aqueous sodium hypochlorite (bleach) was reported in 2011 (Scheme 5.1) [10].

Recyclable reagent **2** is a convenient chlorinating reagent with a reactivity pattern similar to that of (dichloroiodo)benzene. Scheme 5.2 shows several representative chlorinations of organic substrates [10]. The final products are conveniently separated from the polymeric by-product by simple filtration and isolated in

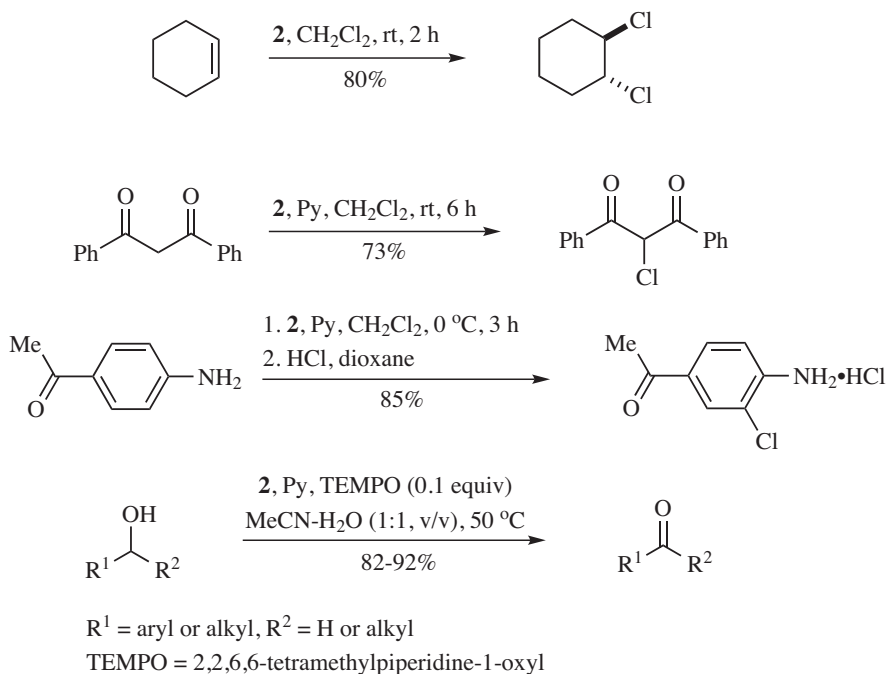
**Scheme 5.1**

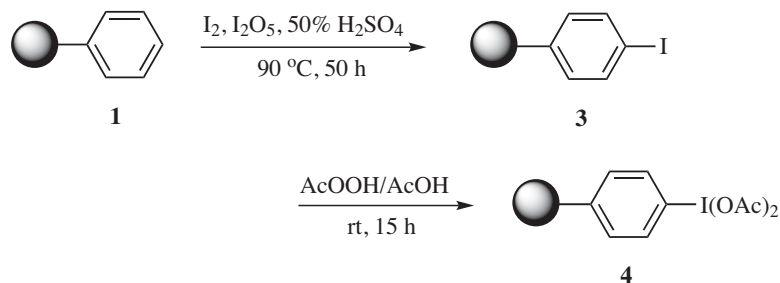
good purity after evaporation of solvent. The polymeric by-product, poly(iodostyrene), can be converted back into reagent **2** by treatment with bleach and aqueous HCl in about 90% overall yield.

The preparation and applications of polystyrene-supported hypervalent iodine(III) reagents bearing (diacetoxy)iido, (dihalo)iido, hydroxy(tosyloxy)iido, hydroxy(phosphoryloxy)iido, aryliodonium and 1,2-benziodoxol-3-one groups were reviewed by Togo and Sakuratani in 2002 [5].

Several variants of polystyrene-supported [bis(acyloxy)iido]arenes have been developed [11–21]. Poly[(diacetoxyiido)styrene] (**4**) can be prepared in two steps from commercial polystyrene **1** with an average molecular weight ranging from 45 000 to 250 000 [11–13, 19–21]. In the first step, polystyrene **1** is iodinated with iodine and iodine pentoxide in sulfuric acid to give poly(iodostyrene) **3**, which is subsequently converted into the diacetate **4** by treatment with peracetic acid (Scheme 5.3) [11, 13]. The loading capacity of the polymeric reagent **4** obtained by this procedure (Scheme 5.3) varies from 2.96 to 3.5 mmol g⁻¹ as measured by iodometry and elemental analysis [11–13].

The original version of reagent **4**, reported by Yokoyama, Togo and coworkers in 1998, is insoluble in organic solvents [12]. An insoluble crosslinked poly[(diacetoxyiido)styrene] has been prepared by a similar

**Scheme 5.2**



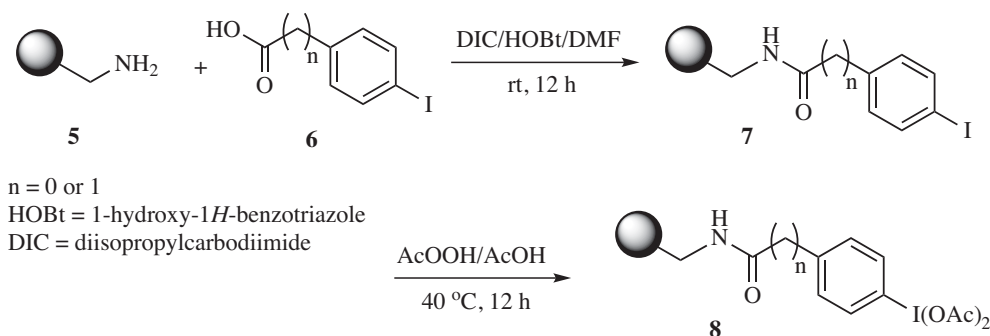
Scheme 5.3

procedure from commercially available 2% crosslinked polystyrene [15, 16]. A soluble version of diacetate **4** can be prepared from linear polystyrene (MW = 250 000) [13].

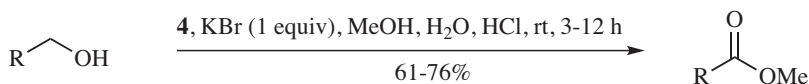
Poly[(diacetoxyiodo)styrene] (**4**) is a convenient, practical application reagent. After reaction with an organic substrate, the iodinated resin can be easily isolated from the reaction mixture by filtration and reoxidized with peracetic acid. Polymer-supported reagent **4** can be reused many times with no loss of activity [14]. Moreover, it can be used as a starting material for the preparation of several other polymer-supported hypervalent iodine reagents, such as polymeric analogs of [bis(trifluoroacetoxy)iodo]benzene [14, 17], iodosylbenzene [22], iodosylbenzene sulfate [23] and [hydroxy(tosyloxy)iodo]benzene [24, 25]. In particular, the polymer-supported [bis(trifluoroacetoxy)iodo]benzene can be prepared by the reaction of diacetate **4** with trifluoroacetic acid [17, 26], or by the oxidation of poly(iodostyrene) (**3**) with 30% $H_2O_2/(CF_3CO)_2O$ [17]. Compared to the diacetate **4**, the polymer-supported [bis(trifluoroacetoxy)iodo]benzene has better solubility in dichloromethane and is a more effective oxidant in the oxidative biaryl coupling reaction of phenol ether derivatives [17].

Polymer-supported (diacetoxyiodo)arenes **8** with a different linker have been prepared from the commercially available aminomethylated polystyrene **5** (Scheme 5.4) [18]. In the first step, the reaction of polymer **5** with 4-iodobenzoic acid (**6**, $n = 0$) or 4-iodophenylacetic acid (**6**, $n = 1$) affords polymer-supported iodides **7** in excellent yield. In the second step, iodides **7** are converted into diacetates **8** by treatment with peracetic acid at $40\text{ }^\circ\text{C}$ overnight [18].

Polymer-supported reagents **8** have a reactivity pattern similar to that of polystyrene derivative **4**. Diacetates **8** are stable for storage and can be regenerated after their use without a measurable loss of activity [18].

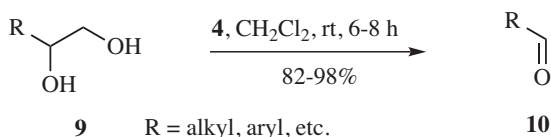


Scheme 5.4



R = C₅H₁₁, cyclohexyl, Ph, EtO₂C(CH₂)₄, etc.

Scheme 5.5



Scheme 5.6

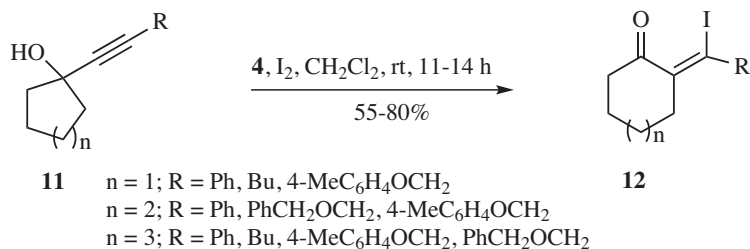
Polymer-supported (diacetoxyiodo)arenes have found broad synthetic application. Poly[(diacetoxyiodo)styrene] (**4**) has been used for the oxidation of alcohols catalyzed by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) [27–30], or in the presence of KBr [31]. In a specific example, primary alcohols are readily oxidized to methyl esters upon treatment with reagent **4** in the presence of KBr in the acidic aqueous methanol solution (Scheme 5.5) [31]. Likewise, organic sulfides are selectively oxidized to the respective sulfoxides by reagent **4** in water in the presence of KBr [32].

Various glycols **9** can be oxidized to aldehydes **10** using reagent **4** at room temperature (Scheme 5.6) [20]. Under these reaction conditions, *cis*-1,2-cyclohexandiol is converted into 1,6-hexandial. Protecting groups, such as OAc, OR, OBn, OBz and isopropylidene, in substrates **9** are compatible with this oxidation [20].

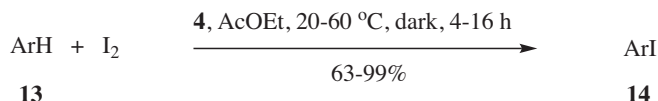
Treatment of 1-alkynylcycloalkanols **11** with reagent **4** and iodine affords (*Z*)-2-(1-iodo-1-organyl)methylenecycloalkanones **12** resulting from the alkoxyl radical-promoted ring-expansion reaction (Scheme 5.7) [33].

Oxidative iodination of aromatic compounds by the combination of a hypervalent iodine reagent with iodine is a synthetically important reaction (Section 3.1.4) [34]. Polymer-supported diacetate **4** is a particularly convenient reagent for oxidative iodination since it can be regenerated and reused many times. Reagent **4** gives the best results for the iodination of electron-rich arenes **13**, with predominant formation of the *para*-substituted products **14** (Scheme 5.8) [12, 21].

The reaction of [bis(acyloxy)iodo]arenes with phenols can lead to various synthetically useful products (Section 3.1.11) [34]. Giannis and coworkers have used polymeric reagents **8** for the oxidation of



Scheme 5.7

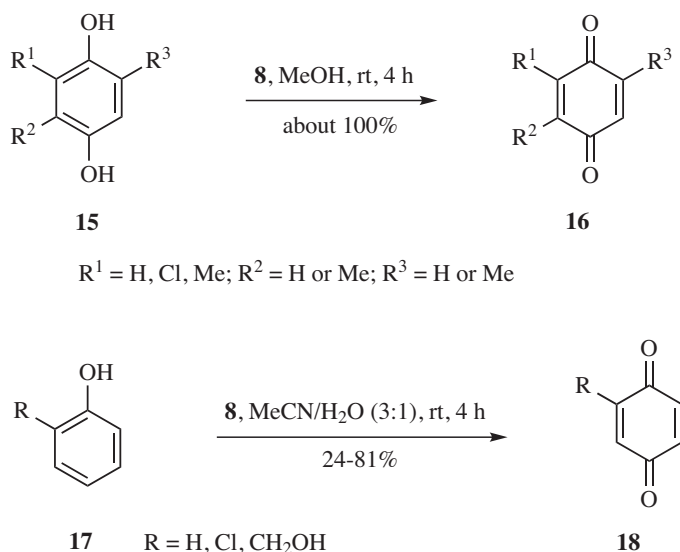


ArH = MeOC₆H₅, HO(CH₂)₂OC₆H₅, 4-BrC₆H₄OMe, Bu^tC₆H₅,
1,3,5-Me₃C₆H₃, 1,3,5-Prⁱ₃C₆H₃, PhC₆H₅, PhOC₆H₅, naphthalene

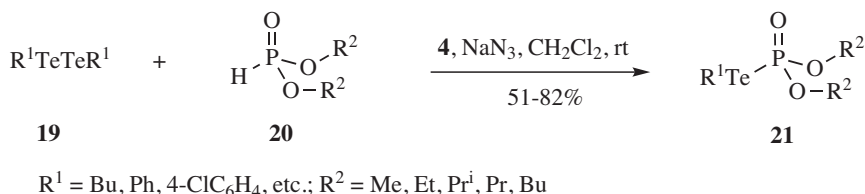
Scheme 5.8

polysubstituted *p*-hydroquinones **15** and phenols **17** to obtain the respective benzoquinones **16** and **18** (Scheme 5.9) [18]. These reactions proceed under mild conditions and resins **8** can be regenerated without a measurable loss of activity. The polystyrene-supported reagent **4** oxidizes various substituted *p*-hydroquinones to benzoquinones in quantitative yields under similar conditions [14]. The oxidation of appropriate phenolic precursors with reagent **4** has been used in the synthesis of the alkaloids (±)-oxomaritidine and (±)-epimaritidine using a multistep sequence of polymer-supported reagents [35].

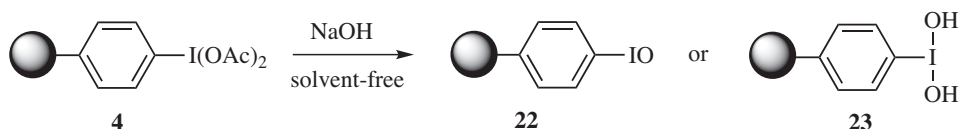
Polymer-supported [bis(acyloxy)iodo]arenes have also been used in the synthesis of numerous heterocyclic systems. Representative examples include the preparation of thiazolo[2,3-*c*]-*s*-triazoles by the reaction of arenecarbaldehyde-4-arylthiazol-2-ylhydrazones with poly[(diacetoxyiodo)styrene] **4** [36], synthesis of 3,4-dihydro-2,1-benzothiazine 2,2-dioxides by oxidative cyclization of 2-arylethanesulfonamides with reagent **4** [37], synthesis of 3,5-disubstituted 1,2,4-thiadiazoles by oxidative dimerization of thioamides using reagent **4** [38], synthesis of isoflavones from 2'-hydroxychalcones using reagent **4** [39, 40], preparation of various 2-substituted 1,3-dioxolanes, 1,3-dioxanes and tetrahydrofurans from alcohols and reagent **4** in the presence of iodine under irradiation conditions [41] and the synthesis of 1-benzoyltetrahydroisoquinoline derivatives using polymer-supported [bis(trifluoroacetoxy)iodo]benzene [42].



Scheme 5.9



Scheme 5.10



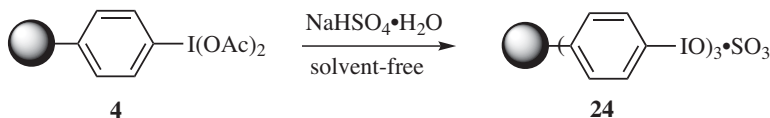
Scheme 5.11

Organyltellurophosphates **21** can be synthesized smoothly in moderate to good yields by the free radical reaction of diorganyl phosphates **20** with diorganyl ditellurides **19** using reagent **4** and sodium azide (Scheme 5.10) [43]; the polymer reagent can be regenerated and recycled with no loss of reactivity.

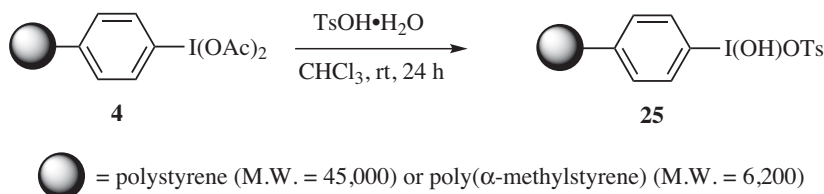
Polystyrene-supported iodosylbenzene (**22**) (loading of $-\text{IO}$ groups up to 1.50 mmol g^{-1}) has been prepared by a solvent-free reaction of poly[(diacetoxyiodo)styrene] (**4**) with sodium hydroxide (Scheme 5.11) [22]. Elemental analysis of polymer **22** indicates that the $-\text{IO}$ groups are partially hydrated as shown in structure **23**. This resin has been successfully used for efficient oxidation of a diverse collection of alcohols to aldehydes and ketones in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Reagent **22** can also be employed as efficient co-catalyst in combination with RuCl_3 in the catalytic oxidation of alcohols and aromatic hydrocarbons, respectively, to the corresponding carboxylic acids and ketones using Oxone[®] as the stoichiometric oxidant [22].

Polystyrene-supported iodosylbenzene sulfate (**24**) (loading of SO_3 0.68 mmol g^{-1}) can be conveniently prepared by treatment of poly[(diacetoxyiodo)styrene] (**4**) with sodium bisulfate monohydrate under solvent-free conditions (Scheme 5.12) [23]. According to elemental analysis diacetate **4** is converted into the sulfate **24** almost quantitatively. Reagent **24** effects clean, efficient oxidation of a wide range of alcohols and sulfides to the corresponding carbonyl compounds or sulfoxides with high conversions under mild conditions [23]. The final products are conveniently separated from the polymeric by-product by simple filtration and isolated in good purity after evaporation of solvent. Recycling of the resin is possible, with minimal loss of activity after several reoxidations.

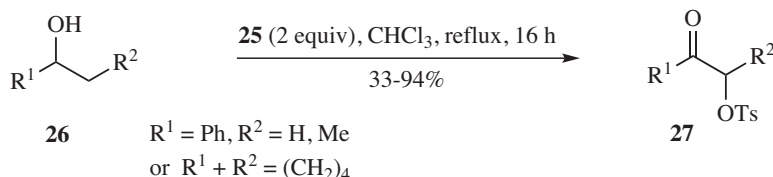
Togo and coworkers have reported the preparation of a recyclable, polystyrene-supported [hydroxy(tosyloxy)iodo]arene (**25**) from the respective poly[(diacetoxyiodo)styrene] (**4**) and *p*-toluenesulfonic acid monohydrate in chloroform at room temperature (Scheme 5.13) [24, 25]. According



Scheme 5.12



Scheme 5.13



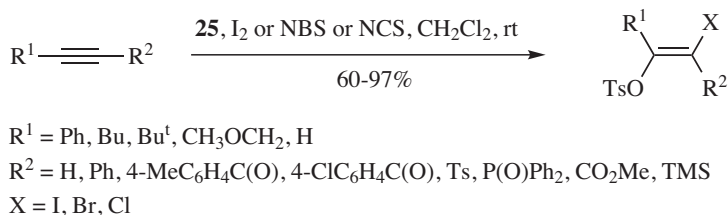
Scheme 5.14

to analytical data, 100% of the (diacetoxi)iodo groups of polymer **4** are converted into the corresponding hydroxy(tosyloxy)iodo groups in product **25** under these reaction conditions.

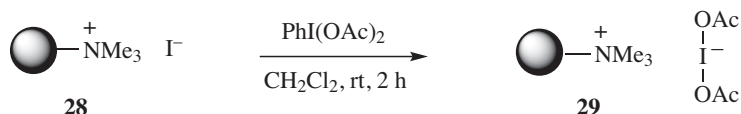
Poly[hydroxy(tosyloxy)iodo]styrene (**25**) shows similar reactivity to the monomeric [hydroxy(tosyloxy)iodo]benzene (HTIB) [44] in the α-tosyloxylation of ketones. Moreover, polymeric reagent **25** can be used for the direct conversion of alcohols **26** into α-tosyloxyketones **27** (Scheme 5.14), while HTIB has a low reactivity toward alcohols [24,25].

In general, poly[hydroxy(tosyloxy)iodo]styrene (**25**) can be used in the same oxidative transformations as the monomeric HTIB [39, 45–48]. In particular, it can serve as an oxidant in the Hofmann-type degradation of carboxamides to the respective amines. In a specific example, primary alkyl- and benzylcarboxamides are converted into the corresponding alkylammonium tosylates by treatment with reagent **25** in acetonitrile at reflux in yields ranging from 60% to 90% [45]. Reagent **25** has been used for direct α-hydroxylation of ketones [46,47] and in the synthesis of isoflavones from 2'-benzoyloxychalcones [39]. Poly[hydroxy(tosyloxy)iodo]styrene (**25**) has also been used in the halotosyloxylation reaction of alkynes with iodine or *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) (Scheme 5.15) [48]. The polymeric reagent can be regenerated and reused numerous times.

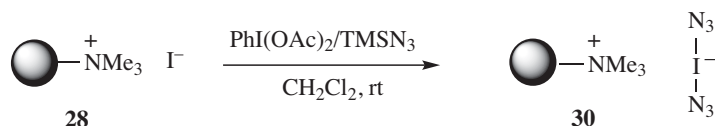
Kirschning and coworkers have developed several polymer-supported halogen-ate(I) complexes [49–53]. Specifically, the polymer-supported diacetoxiodine-ate(I) complex **29** was prepared by the oxidation of polystyrene-bound iodide **28** using (diacetoxiodo)benzene (Scheme 5.16) [49].



Scheme 5.15



Scheme 5.16



Scheme 5.17

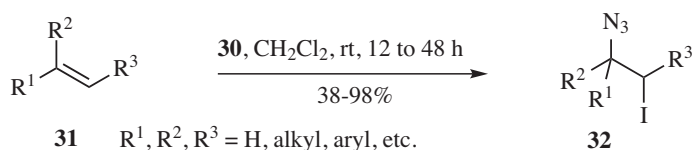
Complex **29** and similar polymer-supported reagents are useful for the electrophilic functionalization of alkenes and for the oxidation of alcohols to carbonyl compounds [49–54].

Kirschning and coworkers have also reported the preparation of reagent systems generated *in situ* from (diazidoiodo)benzene and tetraalkylammonium halides [51]. Particularly useful is a stable polymer-bound bis(azido)iodate (**30**), which can be readily prepared by the reaction of polystyrene-supported iodide **28** with (diazidoiodo)benzene generated *in situ* from (diacetoxyiodo)benzene and azidotrimethylsilane (Scheme 5.17) [51].

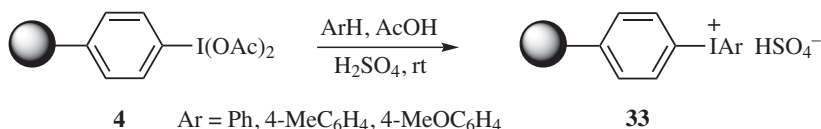
Reagent **30** reacts with alkenes **31** to give the corresponding products of β -azido-iodination (**32**) (Scheme 5.18). These reactions predominantly afford products of *anti*-addition with Markovnikov regioselectivity [51].

Polystyrene-supported diaryliodonium salts **33** can be prepared by the reaction of diacetate **4** with arenes in the presence of sulfuric acid (Scheme 5.19) [55, 56]. Polymer-supported aryl iodonium salts are useful aryl transfer reagents in Pd(II)-catalyzed cross-coupling reactions with salicylaldehydes [56] and aromatic hydrocarbons [55].

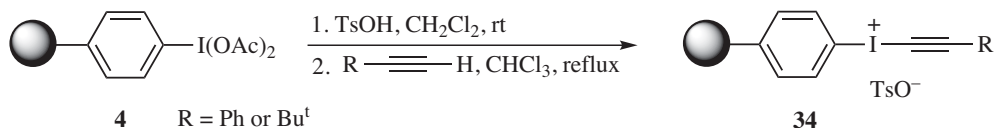
Polymer-supported alkynyliodonium tosylates **34** can be prepared by treatment of reagent **4** with terminal alkynes in the presence of *p*-toluenesulfonic acid (Scheme 5.20) [57]. Polymers **34** are effective alkynylating reagents toward sodium sulfinates and benzotriazole [57].



Scheme 5.18



Scheme 5.19



Scheme 5.20

5.2 Polymer-Supported Iodine(V) Reagents

The first preparation of polymer-supported hypervalent iodine(V) reagents derived from IBX was reported in 2001 [58,59]. Giannis and Mülbaier have developed the aminopropylsilica gel based reagent **35** (Figure 5.1), which can oxidize various primary and secondary alcohols to the respective carbonyl compounds in excellent yields at room temperature in THF under heterogeneous conditions and can be regenerated by oxidation with Oxone without any loss of activity [58]. Rademann and coworkers prepared the polystyrene-based polymeric analog of IBX **36**, which was characterized by IR spectroscopy, elemental analysis and MAS-NMR spectroscopy [59]. Reagent **36** oxidizes various primary, secondary, benzylic, allylic, terpene alcohols

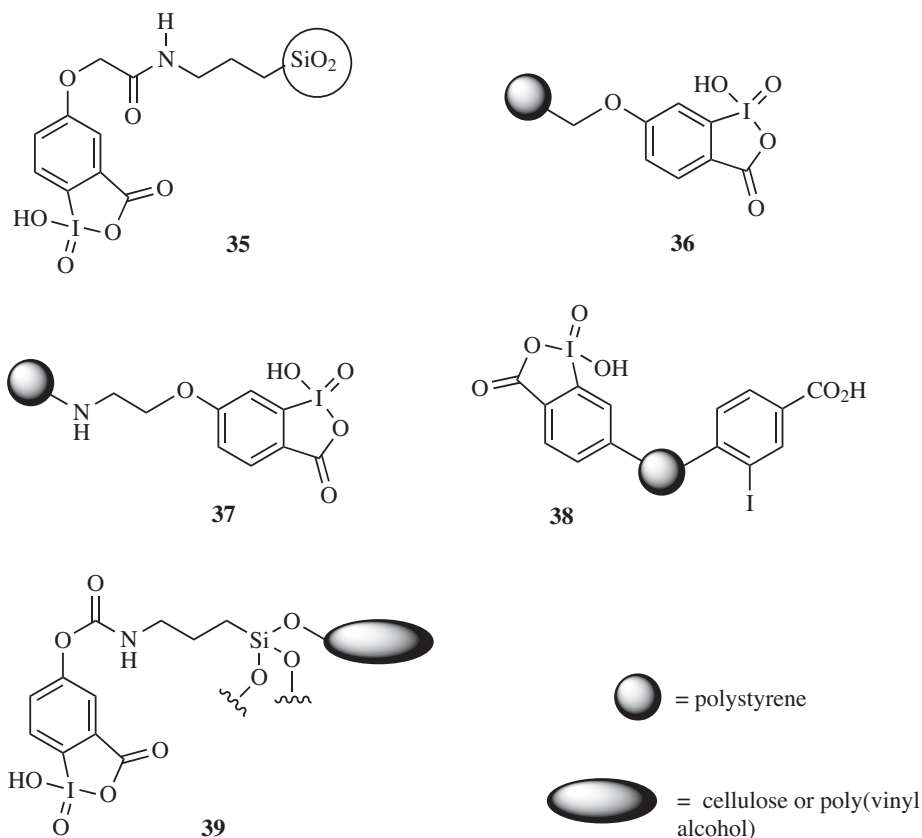


Figure 5.1 Polymer-supported analogs of 2-iodoxybenzoic acid (IBX).

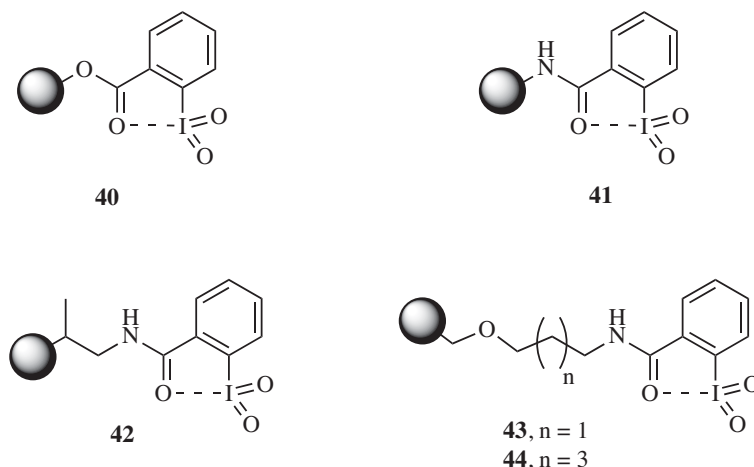
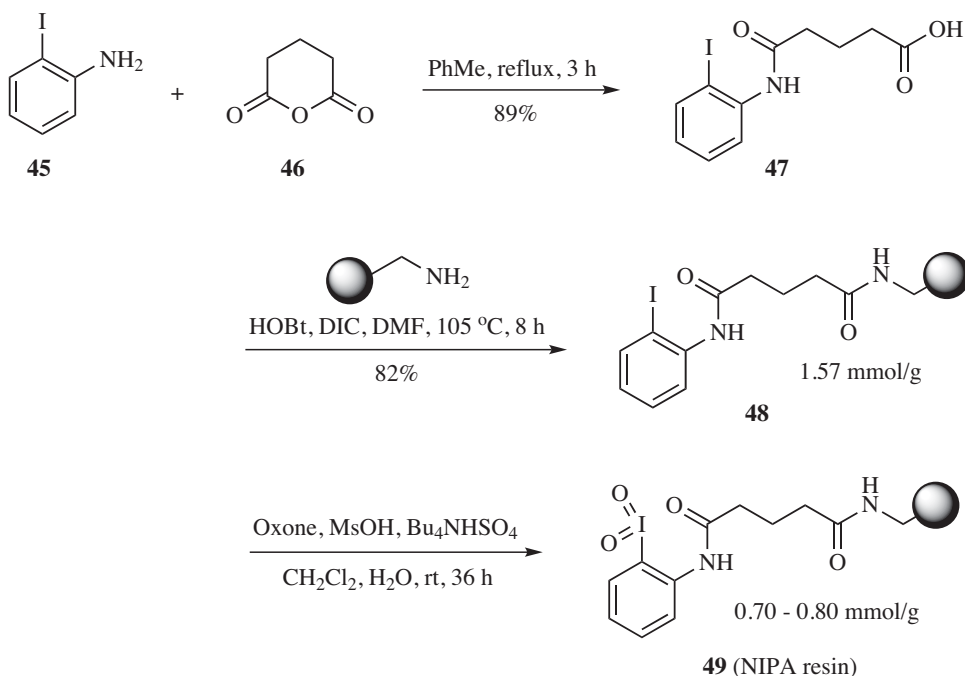


Figure 5.2 Polymer-supported IBX-ester **40** and IBX-amides **41–44**.

and carbamate-protected aminoalcohols to afford the respective aldehydes or ketones in excellent yields – and it can be recycled by repeated oxidation after extensive washings. Lei and coworkers have developed a polymer-supported IBX derivative **37**, which has the advantages of a simplified preparation method and a high oxidation activity of 1.5 mmol g^{-1} [60]. A conceptually different approach was used by Sutherland and coworkers for the preparation of polystyrene-based reagent **38**; in this procedure the iodobenzoic acid moiety was introduced directly to the resin backbone by the iodination/oxidation sequence [61]. The preparation of functional organic–inorganic colloids modified by IBX **39** has been reported by Hatton and coworkers [62].

The presence of a functional group in the *ortho*-position of pseudocyclic iodylarenes (Section 2.2.2) provides an opportunity to link a hypervalent iodine(V) reagent to the polymeric backbone. Lee and coworkers have reported the synthesis of polymer-supported IBX-ester **40** and IBX-amides **41** and **42** (Figure 5.2) starting from commercially available hydroxy or amino polystyrene in two steps [63]. Resins **40–42** were prepared with loadings of $0.65\text{--}1.08 \text{ mmol g}^{-1}$ and were evaluated as oxidants for alcohol substrates. The polymer-supported IBX-amide **42** shows particularly high oxidative activity toward a series of alcohols under mild reaction conditions [63]. IBX-amide resin **42** is also an effective oxidant for oxidative bromination of activated aromatic compounds using tetraethylammonium bromide [64]. Linclau and coworkers reported an improved synthesis of polymer-supported IBX-amide resins **43** and **44** using inexpensive and commercially available 2-iodobenzoic acid chloride and Merrifield resin [65]. Oxidation of alcohols to the corresponding carbonyl compounds can be performed using 1.2 equivalents of the resins **43** and **44**. Recycling of these resins is also possible with minimal loss of activity after two reoxidations [65].

A polymer-supported version of *N*-(2-iodylphenyl)acylamides (NIPA) has been prepared in three simple steps [66]. Commercially available 2-iodoaniline (**45**) was treated with glutaric anhydride (**46**) to give the acid **47**, which was subsequently coupled to aminomethylpolystyrene with 1-hydroxy-1*H*-benzotriazole (HOBt)/diisopropylcarbodiimide (DIC) to give the resin **48**. Oxidation of resin **48** to NIPA resin **49** was performed in a $\text{CH}_2\text{Cl}_2\text{--H}_2\text{O}$ biphasic system using Oxone ($2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$), Bu_4NHSO_4 and methanesulfonic acid (Scheme 5.21). NIPA resin **49** has been shown to effect smooth and efficient oxidation of a broad variety of alcohols to the respective carbonyl compounds [66]. The polymeric material, resulting



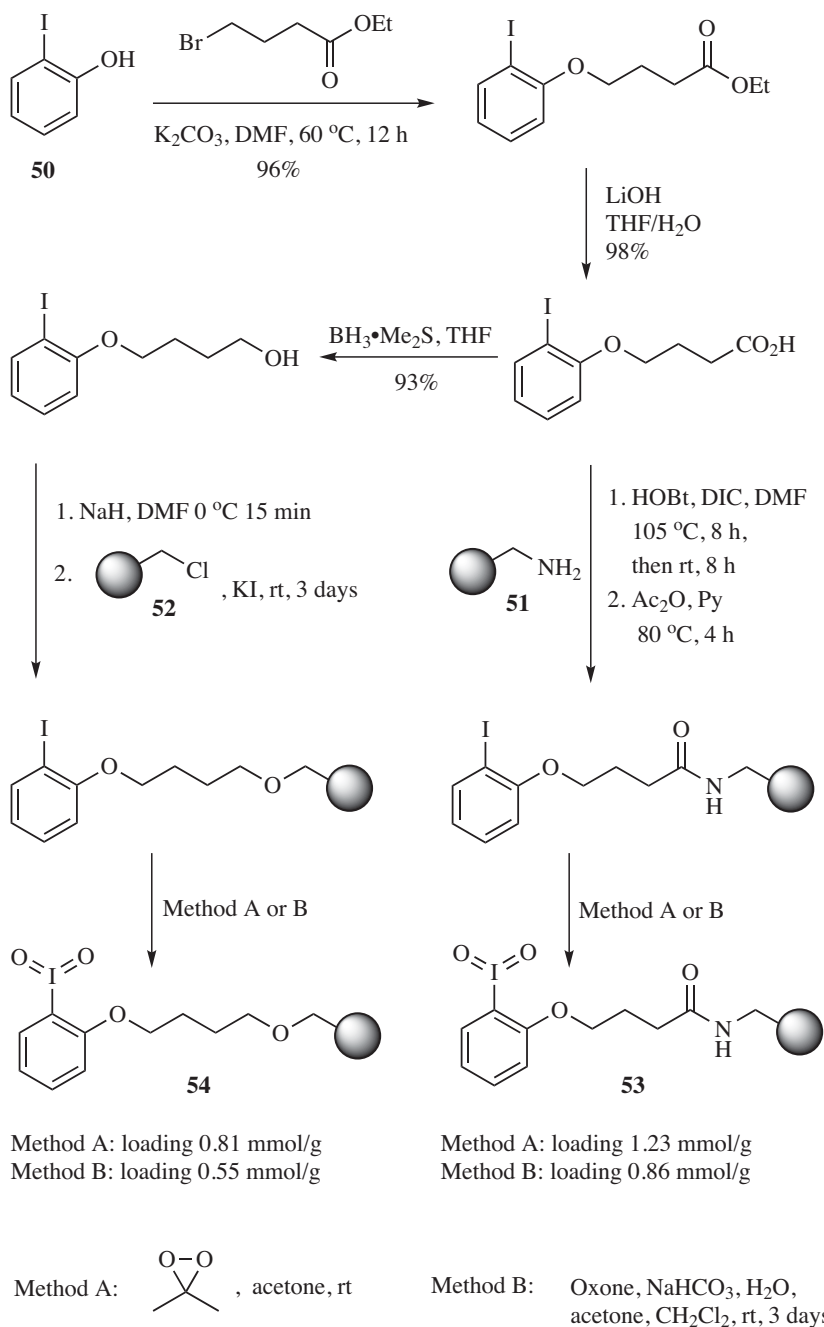
Scheme 5.21

from the reduction of NIPA resin, can be collected and reoxidized. A moderate decline in oxidative activity is observed after multiple recovery steps.

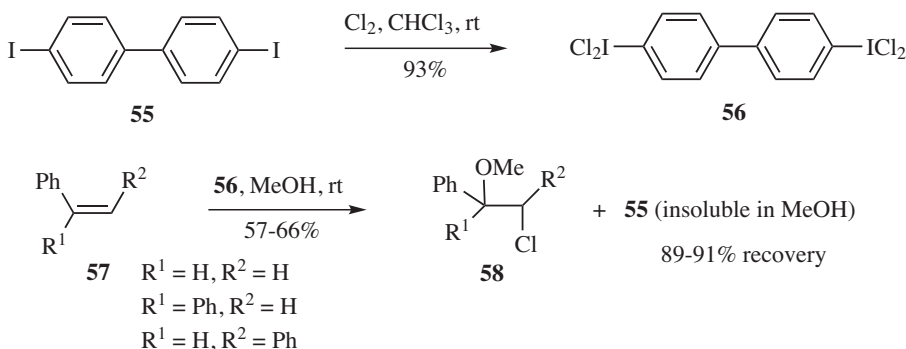
Polymer-supported analogs of 2-iodylphenol ethers, resins **53** and **54** (Scheme 5.22), have been prepared starting from commercially available 2-iodophenol (**50**) and aminomethylated polystyrene **51** or Merrifield resin **52** using 4-hydroxybutanoic acid and 1,4-butanediol, respectively, as linkers. These polymer-supported reagents effect clean, efficient conversion of a wide range of alcohols, including heteroatomic and unsaturated structures, into the corresponding carbonyl compounds. Recycling of the resins is possible with minimal loss of activity after several reoxidations [67].

5.3 Recyclable Nonpolymeric Hypervalent Iodine(III) Reagents

Polymer-supported hypervalent reagents are useful recyclable oxidants, but they have some serious disadvantages compared to nonpolymeric reagents. In particular, polymer-bound reagents often have lower reactivities than the monomeric analogues, the loading of the hypervalent iodine sites is difficult to control and, moreover, repeated use of these resins leads to significant degradation due to benzylic oxidation of the polystyrene chain. The simple, nonpolymeric, recyclable iodonanes have similar reactivity to the original hypervalent iodine(III) reagents and are free of the disadvantages of polymeric reagents. The reduced form of a recyclable nonpolymeric reagent can be effectively recovered from a reaction mixture using one of the biphasic separation techniques discussed in the following subsections.



Scheme 5.22



Scheme 5.23

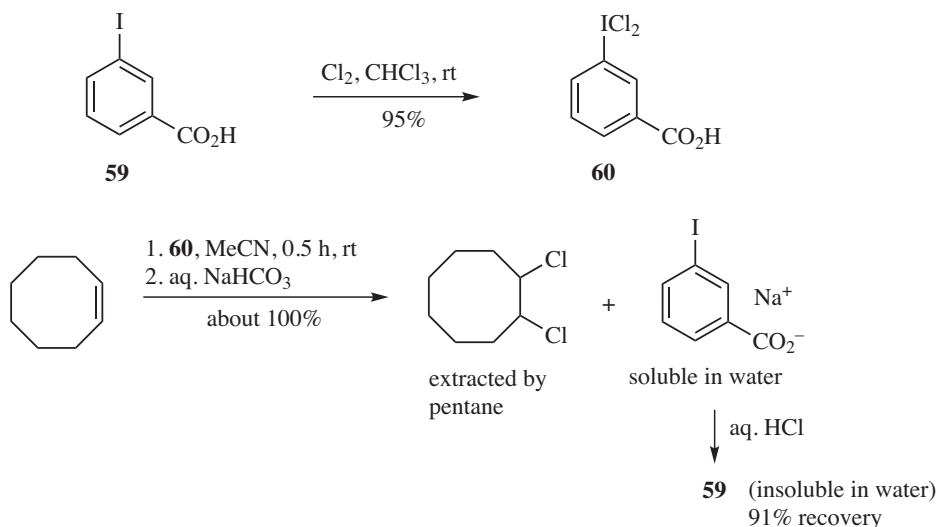
5.3.1 Recyclable Iodine(III) Reagents with Insoluble Reduced Form

Several recoverable hypervalent iodine reagents of this type have been developed since 2004. A recyclable chlorinating reagent, 4,4'-bis(dichloroiodo)biphenyl (**56**), can be prepared in high yield by saturating a solution of 4,4'-diiodobiphenyl (**55**) in chloroform with gaseous chlorine for one hour at room temperature under stirring (Scheme 5.23). Compound **56** is a convenient chlorinating reagent; for example, its reaction with styrene derivatives **57** in methanol affords products of electrophilic chloromethoxylation (**58**) in good yield. The reduced form of reagent **56**, 4,4'-diiodobiphenyl (**55**), is practically insoluble in methanol and can be recovered by simple filtration and used for the regeneration of reagent **56** [68, 69]. 4,4'-Bis(dichloroiodo)biphenyl (**56**) has also been used as a recyclable oxidizing reagent for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds [70], as well as for the preparation of α -azido ketones and esters by direct oxidative azidation of carbonyl compounds using sodium azide as the source of azide anions [71].

Another recyclable chlorinating reagent, 3-(dichloroiodo)benzoic acid (**60**), can be conveniently prepared by the chlorination of commercially available 3-iodobenzoic acid (**59**). A reduced form of reagent **60**, 3-iodobenzoic acid (**59**), can also be easily separated as a solid from the products of chlorination by basic aqueous work-up followed by acidification with HCl [68, 69]. Scheme 5.24 shows an example of a chlorination cycle using reagent **60** [69]. Alternatively, **59** can be separated from the reaction products by treatment with anionic exchange resin AmberliteTM IRA 900 (Section 5.3.2).

A green, recyclable and efficient catalytic system for the oxidation of alcohols and sulfides in water has been developed based on 3-(dichloroiodo)benzoic acid (**60**) as a stoichiometric oxidant and SiO_2 -supported RuCl_3 **61** as the catalyst (Scheme 5.25) [72]. This catalytic oxidative system effects clean and efficient oxidation of a wide range of alcohols to the corresponding aldehydes and ketones, or sulfides to sulfoxides, in high conversions with excellent chemoselectivity, under mild conditions and with an easy work-up procedure. Furthermore, SiO_2 - RuCl_3 catalyst **61** can be recovered by simple filtration and recycled up to six consecutive runs without significant loss of activity. The reduced form of 3-(dichloroiodo)benzoic acid (**60**), 3-iodobenzoic acid (**59**), can be easily separated from reaction mixtures and converted back into reagent **60** by treatment with bleach and aqueous HCl in about 90% overall yield [72].

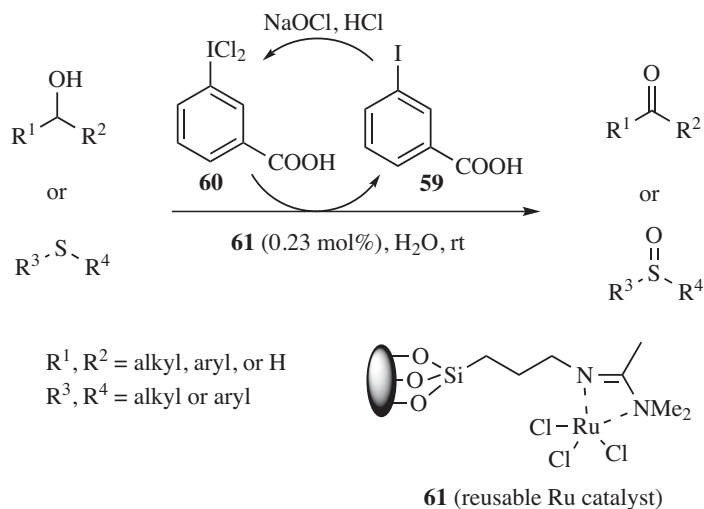
Zhang and Li have reported a convenient preparation of 1-chloro-1,2-benziodoxol-3(1*H*)-one **63** and its application as a recyclable reagent for an efficient TEMPO-catalyzed oxidation of alcohols (Scheme 5.26) [73]. Reagent **63** can be prepared by a convenient, large-scale and high-yielding procedure from 2-iodobenzoic acid (**62**) using sodium chlorite as the stoichiometric oxidant in dilute hydrochloric acid at room temperature. Various alcohols can be oxidized to their corresponding carbonyl compounds in excellent yields using reagent



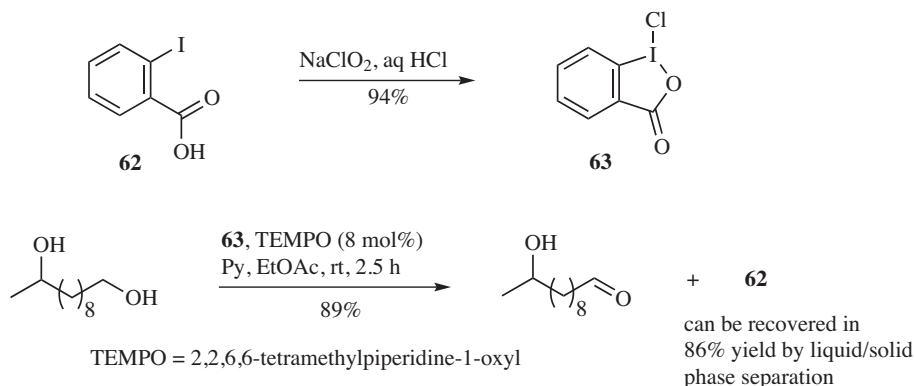
Scheme 5.24

63 as a recyclable reagent in the presence of TEMPO; a primary hydroxy group is preferentially oxidized over a secondary hydroxyl as exemplified in Scheme 5.26. 1-Chloro-1,2-benziodoxol-3(1*H*)-one **63** can be easily recycled after simple solid/liquid-phase separation and the subsequent regeneration sequence [73].

Various recyclable hypervalent iodine reagents based on the frameworks of 1,3,5,7-tetraphenyladamantane (**65–67**) [74], tetraphenylmethane (**69–71**) [75], biphenyl (**73** and **74**) [76] and terphenyl (**76**) [76] have been developed (Figure 5.3). Similarly to previously discussed reagent **56** (Scheme 5.23), aryl iodides **64**, **68**, **72**



Scheme 5.25



Scheme 5.26

and **75**, formed in the reactions of these compounds with organic substrates, are insoluble in methanol and can be recovered by simple filtration.

Recyclable (diacetoxyiodo)arenes **65**, **69**, **73** and **76** (Figure 5.3) are prepared in excellent yields by the oxidation of appropriate iodides **64**, **68**, **72** and **75** using *m*-chloroperoxybenzoic acid (*m*CPBA) in acetic acid [74–76]. The diacetates **65** and **69** can be subsequently converted into the respective

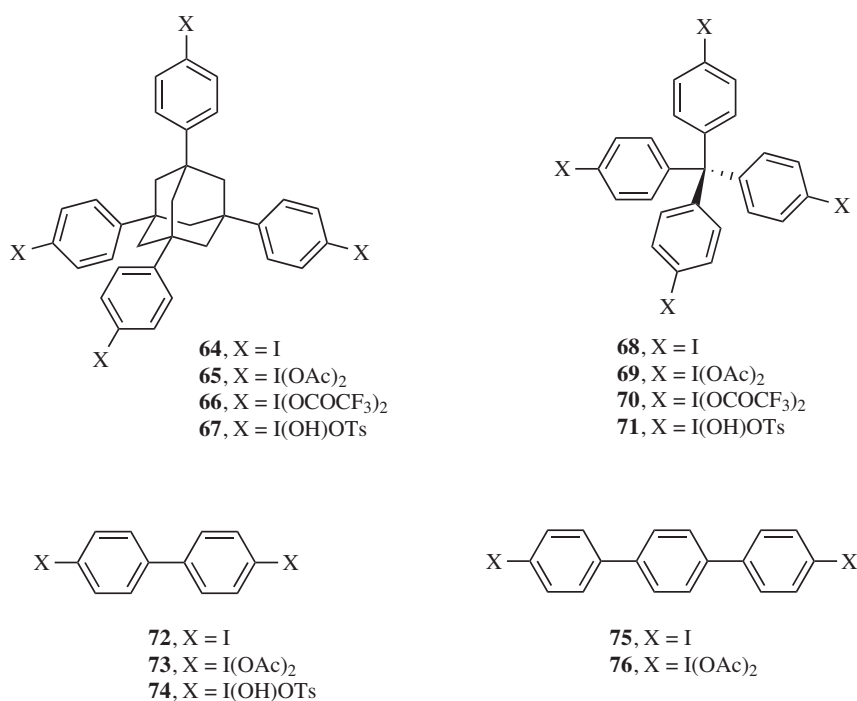
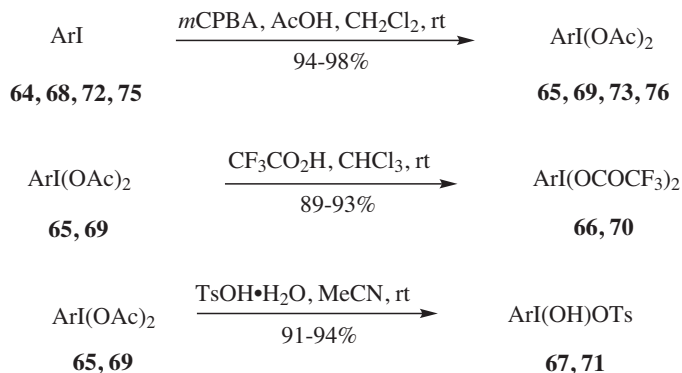


Figure 5.3 Recyclable hypervalent iodine reagents based on the frameworks of 1,3,5,7-tetraphenyladamantane (**65–67**), tetraphenylmethane (**69–71**), biphenyl (structures **73** and **74**) and terphenyl (structure **76**).



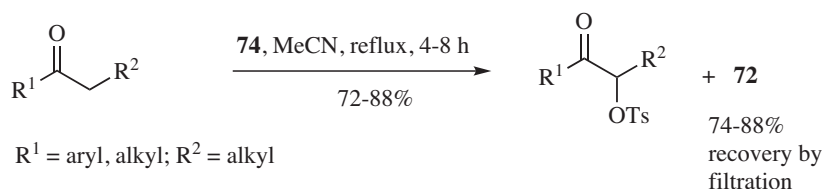
Scheme 5.27

[bis(trifluoroacetoxy)iido]arenes or [hydroxy(tosyloxy)iido]arenes by treatment with trifluoroacetic or toluenesulfonic acids (Scheme 5.27) [74, 75]. The biphenyl-based tosylate **74** is prepared directly from the iodide **72** by oxidation with *m*CPBA in the presence of toluenesulfonic acid [76].

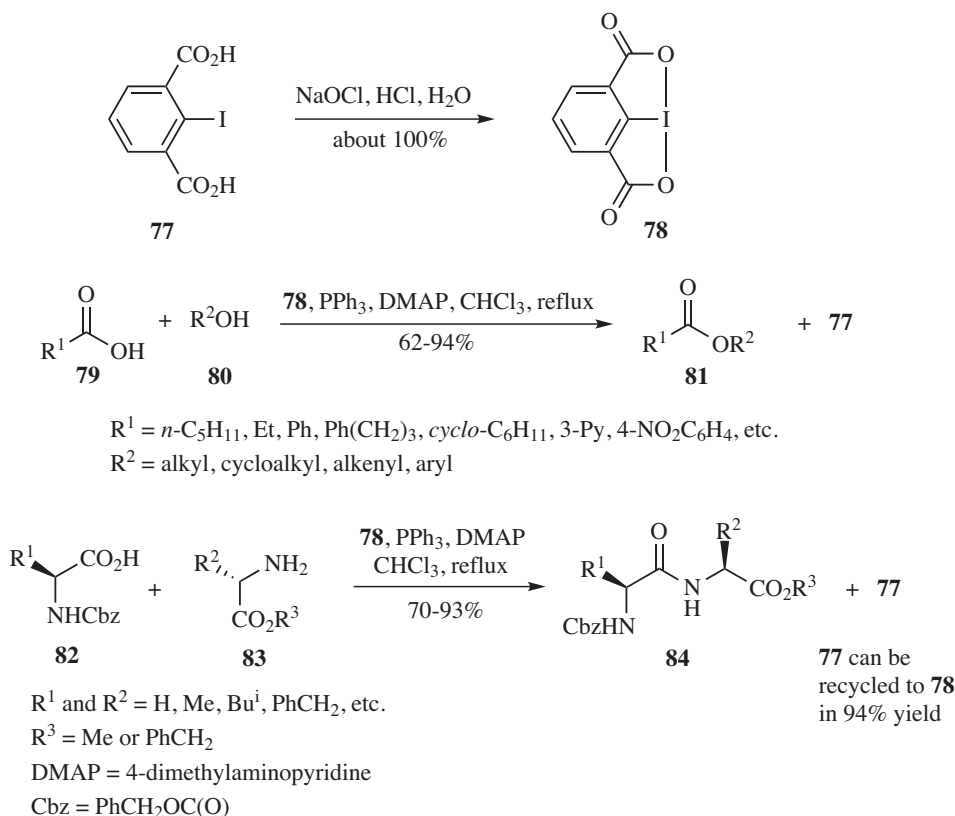
The reactivity pattern of recyclable hypervalent iodine reagents **65–67**, **69–71**, **73**, **74** and **76** is similar to the common iodobenzene-based reagents [34]. For example, the recyclable (diacetoxyiido)arenes **65**, **69**, **73** and **76** can be used instead of (diacetoxyiido)benzene in the KBr or TEMPO-catalyzed oxidations of alcohols [74–78], while [hydroxy(tosyloxy)iido]arenes **67**, **71** and **74** are excellent reagents for tosyloxylation of ketones (Scheme 5.28) [76].

Recyclable [bis(trifluoroacetoxy)iido]arenes **66** and **70** are excellent reagents for oxidative coupling of thiophenes or pyrroles [79] and for direct oxidative cyanation of heteroaromatic compounds using Me₃SiCN as source of cyanide anion [80, 81].

Recyclable reagent **78** can be conveniently prepared in quantitative yield from the commercially available 2-iodoisophthalic acid (**77**) by oxidation with sodium hypochlorite in aqueous hydrochloric acid [82]. Compound **78** is an efficient coupling reagent for the direct condensation between carboxylic acids **79** and alcohols **80** to give the corresponding esters **81** in high yields (Scheme 5.29). Under similar conditions, amines can be coupled with carboxylic acids to provide amides in good yields. This reaction can be used for the racemization-free synthesis of peptides without racemization, as illustrated by the synthesis of dipeptides **84** by coupling of protected amino acids **82** and **83** promoted by reagent **78**. Reagent **78** can be recovered by treatment of the reaction mixture with saturated aqueous NaHCO₃, separation of the aqueous layer containing sodium salt of 2-iodoisophthalic acid **77** and acidification of the aqueous solution with hydrochloric acid followed by hypochlorite oxidation.



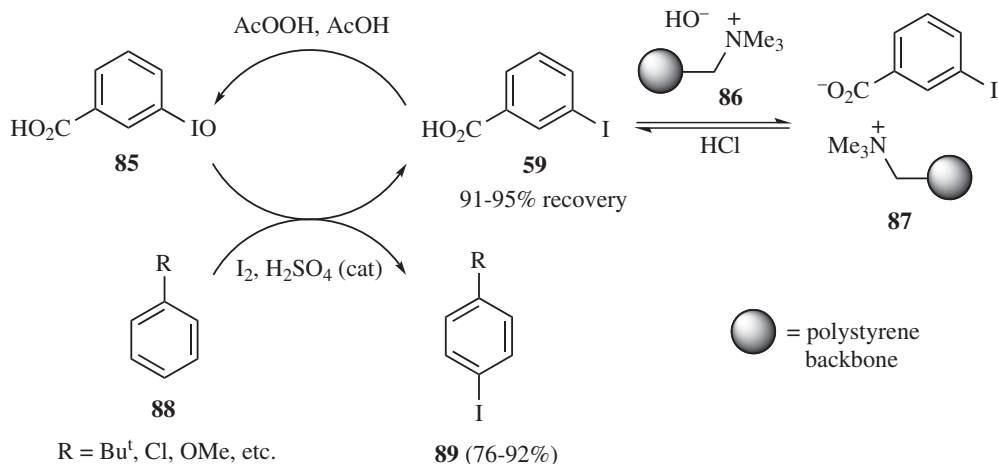
Scheme 5.28



Scheme 5.29

5.3.2 Recovery of the Reduced Form of a Hypervalent Iodine Reagent Using Ion-Exchange Resins

Ion-exchange recycling methodology employs the so-called “tagged” hypervalent iodine reagents [83], the reduced form of which can be removed from the reaction mixture as an anion using anionic ion-exchange resins. Important recyclable hypervalent iodine reagents of this type are represented by 3-iodosylbenzoic acid (**85**) and its derivatives. The tagging approach can be illustrated by the oxidative iodination of aromatic substrates (Scheme 5.30). The iodination of aromatic compounds **88** is performed by treatment with iodine and 3-iodosylbenzoic acid (**85**) in acetonitrile in the presence of catalytic sulfuric acid [84]. The products of iodination **89** are separated from the acidic by-products by treatment with anionic exchange resin Amberlite IRA 900 (hydroxide form) **86** and isolated as pure compounds after evaporation of solvent. The reduced form of the hypervalent iodine oxidant, 3-iodobenzoic acid (**59**), can be easily recovered in 91–95% yield from the Amberlite resin **87** by treatment with aqueous HCl followed by extraction with ethyl acetate. A similar purification and recovery procedure using Amberlite IRA 900 (hydroxide or bicarbonate forms) has been used for the oxidative iodination of alkenes with 3-iodosylbenzoic acid/iodine [84,85], for the α -tosyloxylolation of ketones with 3-iodosylbenzoic acid/toluenesulfonic acid recyclable reagent system [86] and for the selective oxidation of primary and secondary alcohols to the respective carbonyl compounds with 3-iodosylbenzoic acid in the presence of RuCl_3 (0.5 mol%) at room temperature in aqueous acetonitrile [87].

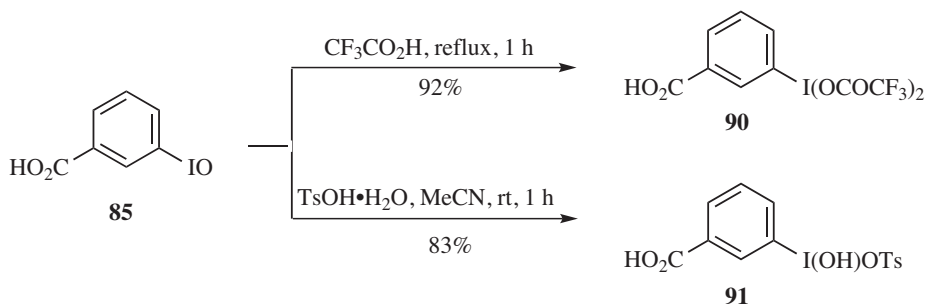


Scheme 5.30

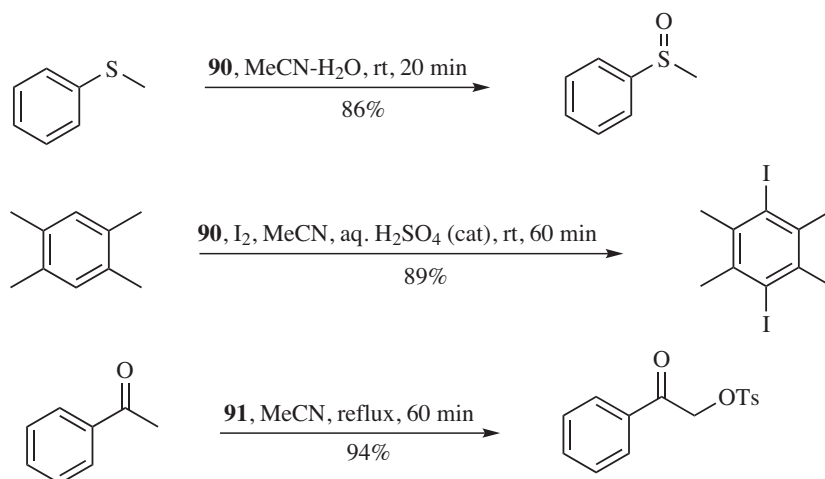
3-Iodosylbenzoic acid (**85**) is also a convenient recyclable hypervalent iodine oxidant for the synthesis of α -iodo ketones by oxidative iodination of ketones [88]. Various ketones and β -dicarbonyl compounds can be iodinated by this reagent system under mild conditions to afford the respective α -iodo substituted carbonyl compounds in excellent yields. The final products of iodination are conveniently separated from by-products by simple treatment with anionic exchange resin Amberlite IRA 900 HCO_3^- and are isolated with good purity after evaporation of the solvent. The reduced form of the hypervalent iodine oxidant, 3-iodobenzoic acid (**59**), can be recovered in 91–95% yield from the Amberlite resin by treatment with aqueous hydrochloric acid followed by extraction with ethyl acetate [88].

Two recyclable nonpolymeric hypervalent iodine reagents, 3-[bis(trifluoroacetoxy)iodo]benzoic acid (**90**) and 3-[hydroxy(tosyloxy)iodo]benzoic acid (**91**) can be conveniently prepared in high yield by treatment of 3-iodosylbenzoic acid (**85**) with trifluoroacetic acid or *p*-toluenesulfonic acid, respectively (Scheme 5.31) [89,90].

The reactivity pattern of compounds **90** and **91** is similar to common hypervalent iodine reagents, as illustrated by their use for the oxidation of sulfides, oxidative iodination of arenes and α -tosyloxylation of ketones (Scheme 5.32) [89]. The products of all these reactions can be conveniently separated from the by-product, 3-iodobenzoic acid, by simple treatment with ion-exchange resin IRA-900 according to



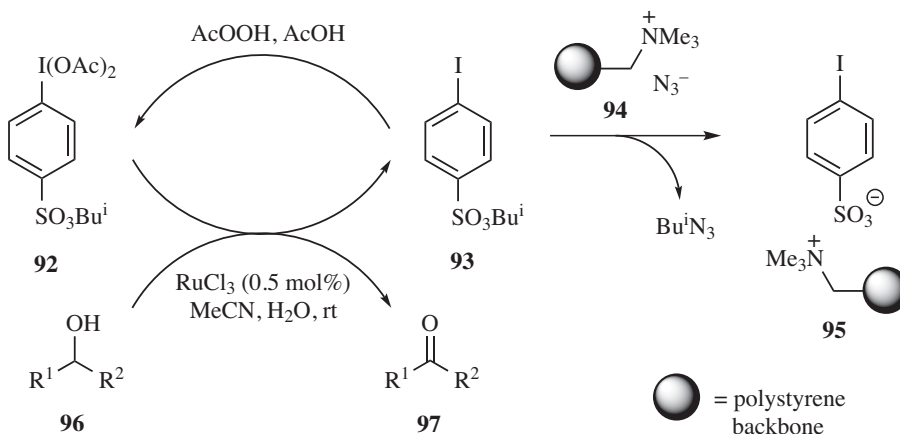
Scheme 5.31



Scheme 5.32

Scheme 5.30. 3-Iodobenzoic acid can be regenerated from IRA 900 resin by treatment with aqueous HCl and can be reoxidized to reagent **77** without additional purification. An alternative procedure for product separation involves basic aqueous work-up followed by acidification with HCl (Section 5.3.1).

A different tagging approach using a phenylsulfonate-tagged (diacetoxyiodo)benzene **92** has been developed by Kirschning and coworkers [91]. This approach is based on ion exchange and is initiated by an azide-promoted S_N2 -reaction of isobutyl sulfonate **93** with the N_3^- -resin **94** followed by trapping of the resulting aryl sulfonate anion with the ion-exchange resin. The trapped iodine reagent **93** can be recovered from the resin **95**. This concept has been successfully employed for the $RuCl_3$ -catalyzed oxidation of alcohols **96** to the respective carbonyl compounds **97** (Scheme 5.33), as well as for the glycosidation of thioglycosides and the Suarez reaction of pyranoses [91, 92].



Scheme 5.33

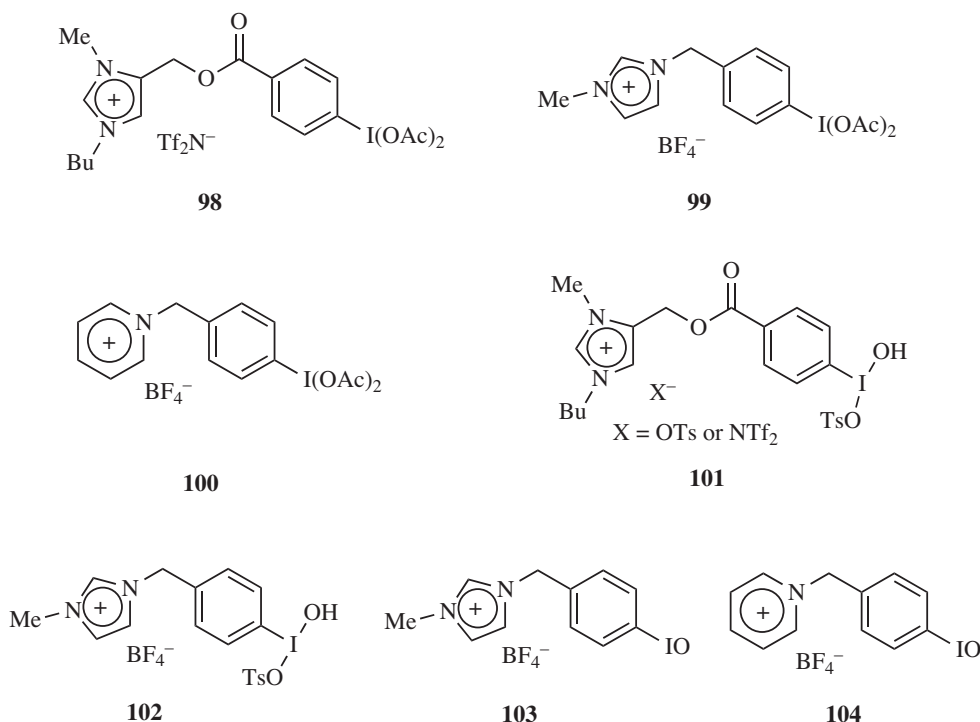


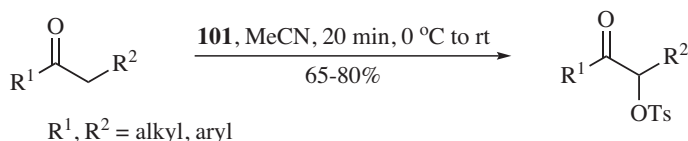
Figure 5.4 Recyclable ion-supported hypervalent iodine(III) reagents.

5.3.3 Ionic-Liquid-Supported Recyclable Hypervalent Iodine(III) Reagents

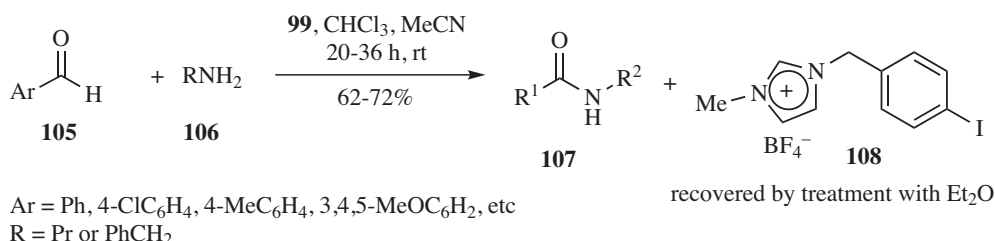
Figure 5.4 shows several examples of ionic-liquid-supported (also called ion-supported) hypervalent iodine(III) reagents [93]. Ion-supported (diacetoxyiodo)arenes **98–100** are prepared by the peracetic oxidation of appropriate ion-supported aryl iodides [93–95]. The ion-supported tosylates **101** and **102** are made by treatment of the appropriate acetates with toluenesulfonic acid in acetonitrile [95, 96] and the ion-supported iodosylbenzenes **103** and **104** are prepared by treatment of appropriate diacetates with sodium hydroxide in water [93]. Ion-supported derivatives **98–104** are thermally stable solids or viscous liquids that can be used as efficient recyclable hypervalent iodine(III) reagents. Reactions of these reagents with organic substrates produce the corresponding ion-supported aryl iodides as by-products, which can be easily recovered from the reaction mixture either by extraction into an ionic liquid phase or by simple filtration.

Various primary and secondary alcohols can be oxidized to aldehydes and ketones with the ion-supported [bis(acyloxy)iodo]arene **99** in the ionic liquid $[\text{emim}]^+[\text{BF}_4]^-$ (1-ethyl-3-methylimidazolium tetrafluoroborate) in the presence of bromide anion [94], or in water in the presence of ion-supported TEMPO [97]. Under similar conditions reagent **99** can be used for mild, efficient, highly selective and environmentally friendly oxidation of aliphatic and aromatic sulfides to sulfoxides in excellent yields [98]. This reaction is compatible with hydroxyl, nitrile, methoxy, carbon–carbon double bonds and ester functionalities. The analogous pyrrolidinium-derived ion-supported [bis(acyloxy)iodo]arenes are efficient oxidants of alcohols to carbonyl compounds in the presence of TEMPO [99].

Likewise, the α -tosyloxylation of ketones with ion-supported [hydroxy(tosyloxy)iodo]arenes **101** proceeds smoothly in acetonitrile even at 0 °C (Scheme 5.34) [95]. These reactions are faster than those with



Scheme 5.34



Scheme 5.35

$\text{PhI}(\text{OH})\text{OTs}$, probably due to the presence of the electron-withdrawing ester group on the benzene ring of reagent **101**.

A metal-free direct oxidative preparation of amides **107** from aldehydes **105** and amines **106** using the ion-supported hypervalent iodine(III) reagent **99** as a recyclable oxidant under mild conditions has been reported (Scheme 5.35) [100]. The oxidant and its reduced form **108** are completely insoluble in diethyl ether; consequently, products **107** can be extracted directly from the reaction mixture and the reagent **99** can be easily recycled.

Charette and coworkers have developed tetraarylphosphonium (TAP)-supported (diacetoxyiodo)benzene **109** (Figure 5.5), which can be used as a recyclable reagent or a catalyst for the α -acetoxylation of ketones [101]. Similarly to the imidazolium-supported [bis(acyloxy)iodo]arene **99**, the reduced form of the TAP-supported reagent **109** can be recovered from the reaction mixture by simple filtration after treatment with ether.

5.3.4 Magnetic Nanoparticle-Supported Recyclable Hypervalent Iodine(III) Reagent

The magnetic nanoparticle-supported (diacetoxyiodo)benzene **114** has been prepared in three steps starting from 4-iodobenzoic acid (Scheme 5.36) [102]. The organic silane groups were used for immobilization of

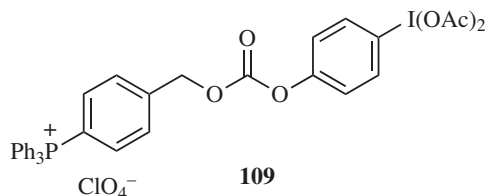
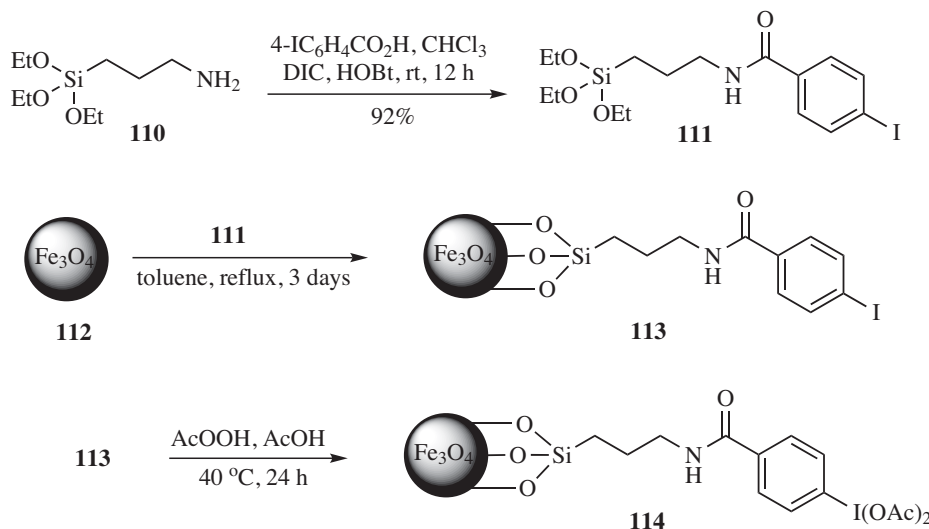


Figure 5.5 Recyclable tetraarylphosphonium (TAP)-supported (diacetoxyiodo)benzene.



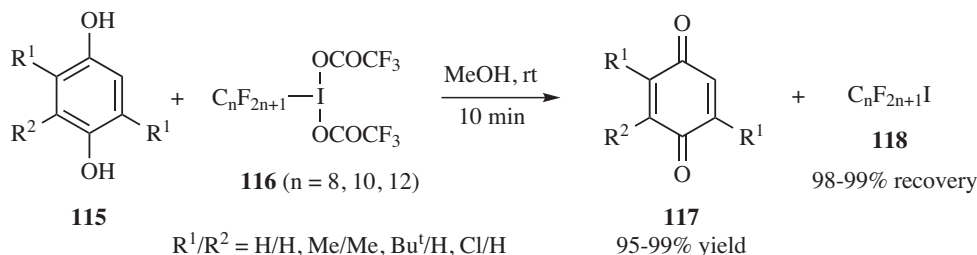
Scheme 5.36

iodobenzene groups to the surface of magnetite nanoparticles, because silanes have a large affinity for under-coordinated surface sites of metal oxide particles. The reaction of 3-aminopropyltriethoxysilane (**110**) with 4-iodobenzoic acid using *N,N*-diisopropylcarbodiimide (DIC) in combination with 1-hydroxybenzotriazole (HOBT) afforded product **111** in excellent yields. Polyvinylpyrrolidone-protected magnetic nanoparticles **112** of 8–20 nm size were prepared by coprecipitation of iron(III) and iron(II) ions in basic solution. The obtained nanoparticles **112** were sonicated for one hour before being treated with excess of compound **111** in anhydrous toluene under reflux to give the magnetic nanoparticle-supported iodobenzene **113**. Subsequent oxidation of product **113** using freshly prepared peracetic acid at 40 °C overnight afforded the diacetate derivative **114** with a loading of 0.68 mmol g⁻¹ as determined by elemental analysis.

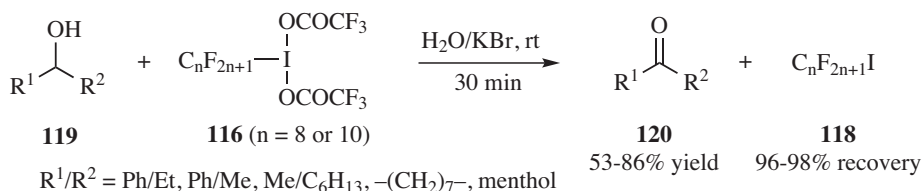
The magnetic nanoparticle reagent **114** can be used for efficient oxidation of a wide range of benzylic, allylic, heterocyclic, alicyclic and aliphatic alcohols to the corresponding aldehydes or ketones in excellent yield. Product separation can be achieved by simple decantation of the organic layer with the assistance of an external magnet. The separated magnetic material **113** is then washed and regenerated by treatment with peracetic acid. The reagent can be recycled many times with no apparent loss of activity [102].

5.3.5 Fluorous Recyclable Hypervalent Iodine(III) Reagents

Tesevic and Gladysz have demonstrated the utility of [bis(trifluoroacetoxy)iodo]perfluoroalkanes C_nF_{2n+1}I(OCOCF₃)₂ with a long fluorous alkyl chain (*n* = 7–12) as convenient recyclable oxidants [103, 104]. Similarly to [bis(trifluoroacetoxy)iodo]benzene, [bis(trifluoroacetoxy)iodo]perfluoroalkanes **116** can serve as excellent reagents for the oxidation of phenolic substrates (Scheme 5.37). The reduced form of the reagents, the respective iodoperfluoroalkanes **118**, can be efficiently separated from the reaction mixture using fluorous techniques and reused. In a specific example, reagents **116** (*n* = 8, 10, 12) can rapidly oxidize 1,4-hydroquinones **115** to afford quinones **117** in methanol at room temperature (Scheme 5.37). Subsequent addition of a fluorous solvent, such as perfluoro(methylcyclohexane), results in a liquid/liquid biphasic system.



Scheme 5.37



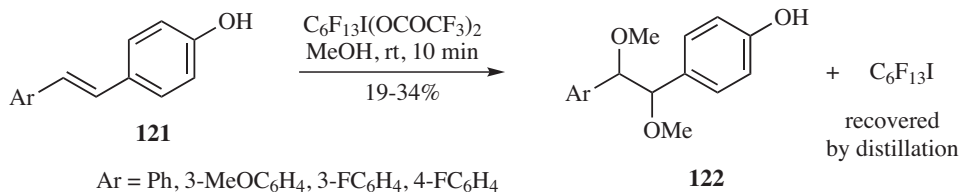
Scheme 5.38

The product quinones **117** are generally isolated in about 95% yields from the methanol phase and iodoperfluoroalkanes **118** are isolated in 98–99% yields from the fluorous phase. The recovered iodoperfluoroalkanes **118** may be reoxidized by peroxytrifluoroacetic acid to give initial reagents **116** in high yield [104]. A convenient new procedure for the oxidation of iodoperfluoroalkanes **118** to [bis(trifluoroacetoxy)iodo]perfluoroalkanes **116** using Oxone (2KHSO₅·KHSO₄·K₂SO₄) in the presence of trifluoroacetic acid has been reported [105].

[Bis(trifluoroacetoxy)iodo]perfluoroalkanes are effective recyclable reagents for the oxidation of aliphatic and benzylic secondary alcohols **119** to ketones **120** in the presence of KBr in aqueous solution (Scheme 5.38) [103]. The reduced form of the reagent, the respective iodoperfluoroalkanes **118**, can be efficiently isolated from the reaction mixture in 96–98% yield by adding three to five volumes of methanol and separating the resulting fluorous/methanolic liquid/liquid biphasic system. The recovered iodoperfluoroalkanes **118** can be reoxidized to reagents **116** and reused [103].

The fluorous bis(trifluoroacetates) **116** (Scheme 5.38) oxidize secondary alcohols in the presence of bromide ions much more rapidly than the common hypervalent iodine(III) reagents, such as iodosylbenzene or (diacetoxyiodo)benzene. The higher reactivity may be due to the directly bound electron-withdrawing perfluoroalkyl substituents in compounds **116**, which enhance their oxidizing strength [103].

Westwell and coworkers investigated the oxidation of hydroxylated stilbenes **121** using [bis(trifluoroacetoxy)iodo]perfluorohexane (Scheme 5.39) [106]. Instead of the expected products of the



Scheme 5.39

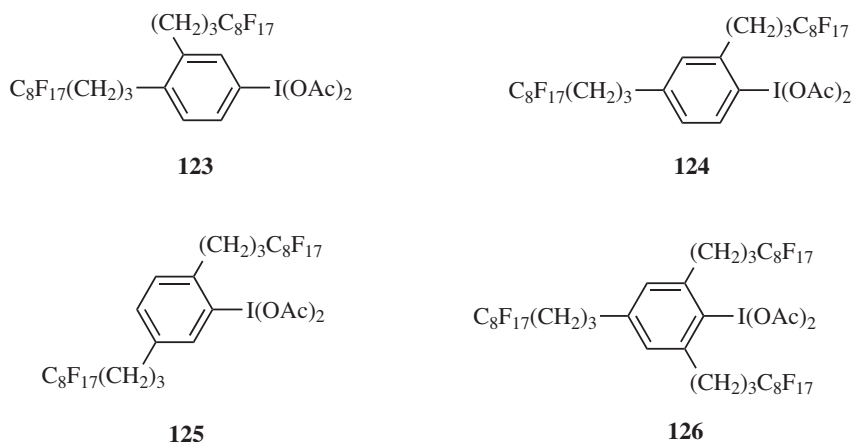


Figure 5.6 Recyclable fluorous (diacetoxyiodo)arenes.

phenolic oxidation, diaryl-1,2-dimethoxyethanes **122** as mixtures of diastereoisomers were isolated from this reaction in moderate yields. The perfluorohexyl iodide by-product (bp 140°C) could be recovered simply by distillation of the reaction mixture under reduced pressure [106].

Gladysz and Rocaboy have reported the application of fluorous (diacetoxyiodo)arenes **123–126** (Figure 5.6) in oxidations of hydroquinones to quinones; in this procedure the fluorous reagents can be conveniently recovered by simple liquid/liquid biphasic workups [107].

Likewise, the series of fluorous (dichloriodo)arenes **127–129** and alkyl iodine(III) dichlorides **130–132** (Figure 5.7) have been prepared in 71–98% yields by reactions of the corresponding fluorous iodides with chlorine [69]. These compounds are effective reagents for the chlorination of alkenes (e.g., cyclooctene) and aromatic compounds (e.g., anisole, 4-*tert*-butylphenol and acetophenone). The organic chlorinated products and fluorous iodide co-products are easily separated by organic/fluorous liquid/liquid biphasic workups. The fluorous iodides can be recovered in 90–97% yields and reoxidized with chlorine [69].

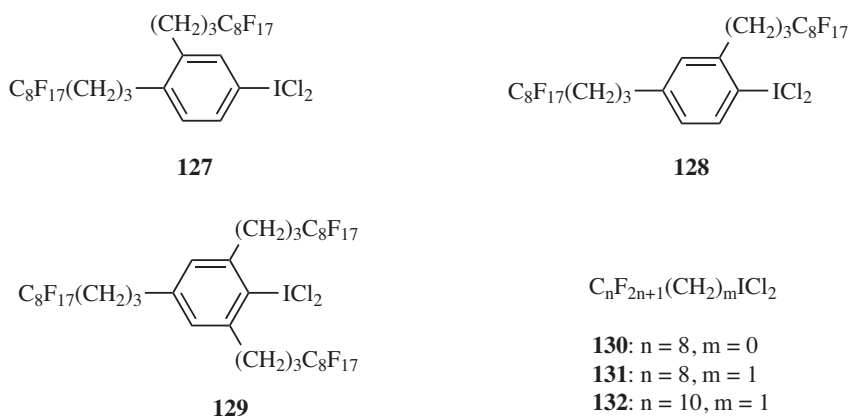
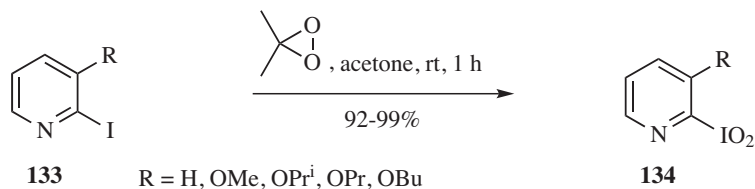


Figure 5.7 Recyclable fluorous aryl- and alkyl iodine(III) dichlorides.



Scheme 5.40

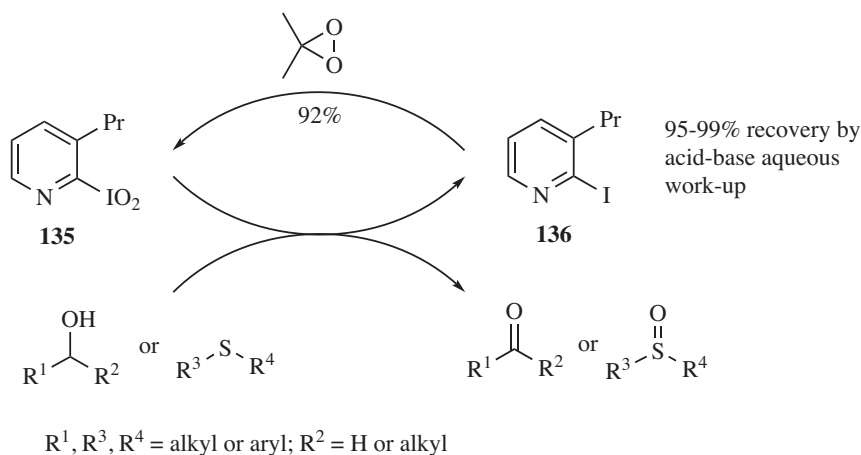
5.4 Recyclable Nonpolymeric Hypervalent Iodine(V) Reagents

The most important and practically useful hypervalent iodine(V) reagents, IBX and DMP, have a serious disadvantage with respect to the principles of green chemistry since they are normally used as the non-recyclable, stoichiometric reagents. In the only available report, it has been shown that IBX can be recovered in a low yield (about 50%) after reaction with alcohols in ethyl acetate [108].

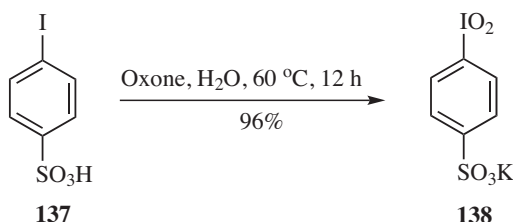
The first nonpolymeric recyclable hypervalent iodine(V) reagents based on the readily available derivatives of 2-iodopyridine were reported in 2011 [109]. 2-Iodylpyridines **134** were prepared by oxidation of the respective 2-iodopyridines **133** with 3,3-dimethyldioxirane (Scheme 5.40). Structures of 2-iodylpyridines **134** ($\text{R} = \text{H, OPr}^i$ and OBu) were established by single crystal X-ray crystallography [109].

2-Iodyl-3-propoxypyridine (**136**) has moderate solubility in organic solvents (e.g., 1.1 mg ml^{-1} in acetonitrile) and it can be used as a recyclable reagent for the oxidation of sulfides to sulfoxides and alcohols to the respective carbonyl compounds (Scheme 5.41) [109]. The reduced form of this reagent, 2-iodo-3-propoxypyridine (**135**), can be effectively separated from the reaction mixture by treatment with diluted sulfuric acid and recovered from the acidic aqueous solution by adding aqueous sodium hydroxide.

Another recyclable hypervalent iodine(V) reagent, potassium 4-iodylbenzenesulfonate (**138**), was prepared by the oxidation of 4-iodobenzenesulfonic acid (**137**) with Oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) in water (Scheme 5.42) [110]. A single-crystal X-ray structure analysis of product **138** revealed the presence of polymeric chains in the solid state due to a combination of numerous intra- and intermolecular interactions.



Scheme 5.41

**Scheme 5.42**

Potassium 4-iodobenzenesulfonate (**138**) is a thermally stable and water-soluble hypervalent iodine(V) oxidant that is particularly useful as a reagent for oxidative iodination of aromatic substrates [110]. Reagent **138** can be effectively recovered from the reaction mixture (92% recovery) after removal of organic products by treatment of the aqueous layer with Oxone at 60 °C for 2 h, followed by filtration of the precipitate of compound **138**.

5.5 Recyclable Iodine Catalytic Systems

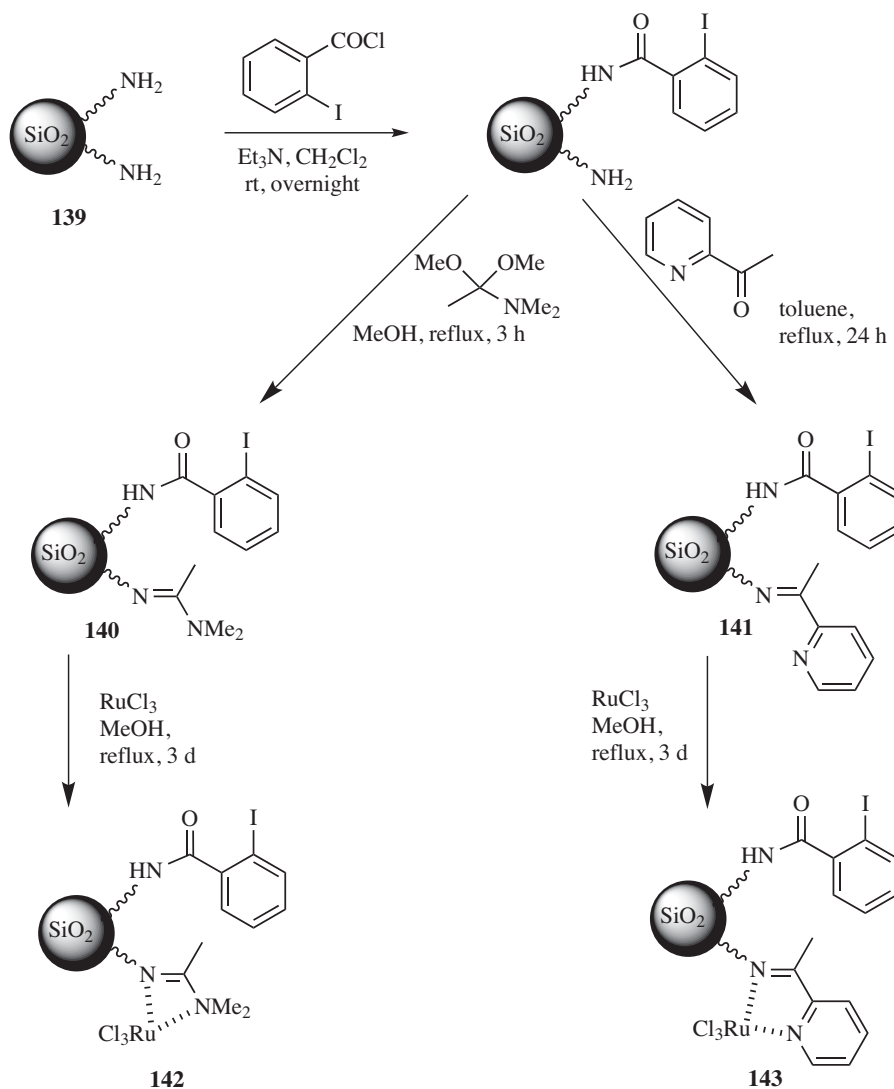
Polymer-supported iodanes and iodoarenes can in principle be used as recyclable catalysts. For example, polystyrene-supported iodosylbenzene (**22**) (Section 5.1) has been employed as an efficient co-catalyst in combination with RuCl_3 in the catalytic oxidation of alcohols and aromatic hydrocarbons, respectively, to the corresponding carboxylic acids and ketones using Oxone as the stoichiometric oxidant [22].

Polystyrene-supported iodobenzene has been used instead of iodobenzene as a catalyst for the α -tosyloxylation of ketones and alcohols with *m*CPBA and *p*-toluenesulfonic acid [111]. In particular, two kinds of polymer-supported PhI, the standard linear poly(4-iodostyrene) and the macroporous crosslinked poly(4-iodostyrene), have been used as recyclable catalysts, which could be recovered from the reaction mixture by simple filtration in 90–100% yield. Recovered poly(4-iodostyrene) could be reused for the same reaction to provide the corresponding α -tosyloxyketone in good yields [111]. Recyclable ionic-liquid-supported iodoarenes have also been used as catalysts in the α -tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid [112].

The polymeric silica materials derived from silylated aryl iodides have been prepared via sol–gel processes, either by the hydrolytic polycondensation of a bis-silylated monomer or by the co-gelification of a monosilylated precursor with tetraethyl orthosilicate [113]. These silica-supported aryl iodides have been successfully applied as supported catalysts in the α -tosyloxylation of aliphatic ketones in the presence of *m*-chloroperbenzoic acid as an oxidant, with the corresponding α -tosyloxyketones obtained in moderate to good isolated yields. The supported catalysts can be recycled by a simple filtration [113].

Particularly useful are bifunctional catalytic systems, which have the iodoarene moiety and a co-catalyst, such as a complex of transition metal, attached to the same polymeric backbone. Efficient recyclable bifunctional catalysts bearing SiO_2 -supported RuCl_3 and iodoarene moieties have been developed and used for environmentally benign oxidation of alcohols or alkylarenes at the benzylic position [114].

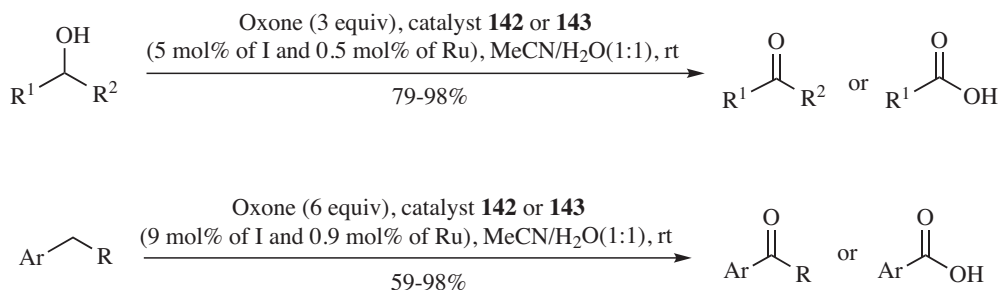
The synthesis of SiO_2 -supported iodoarene– RuCl_3 bifunctional catalysts **142** and **143** consists of building a suitable ligand structure, **140** or **141**, on the surface of commercial aminopropyl silica **139**, followed by complexation with RuCl_3 (Scheme 5.43) [114]. The amounts of RuCl_3 and iodine loaded on the surface of silica gel were determined by elemental analyses of chlorine and iodine. The loadings of iodine and ruthenium for catalyst **142** are 0.60 and 0.06 mmol g^{-1} and for catalyst **143** 0.62 and 0.05 mmol g^{-1} , respectively. For



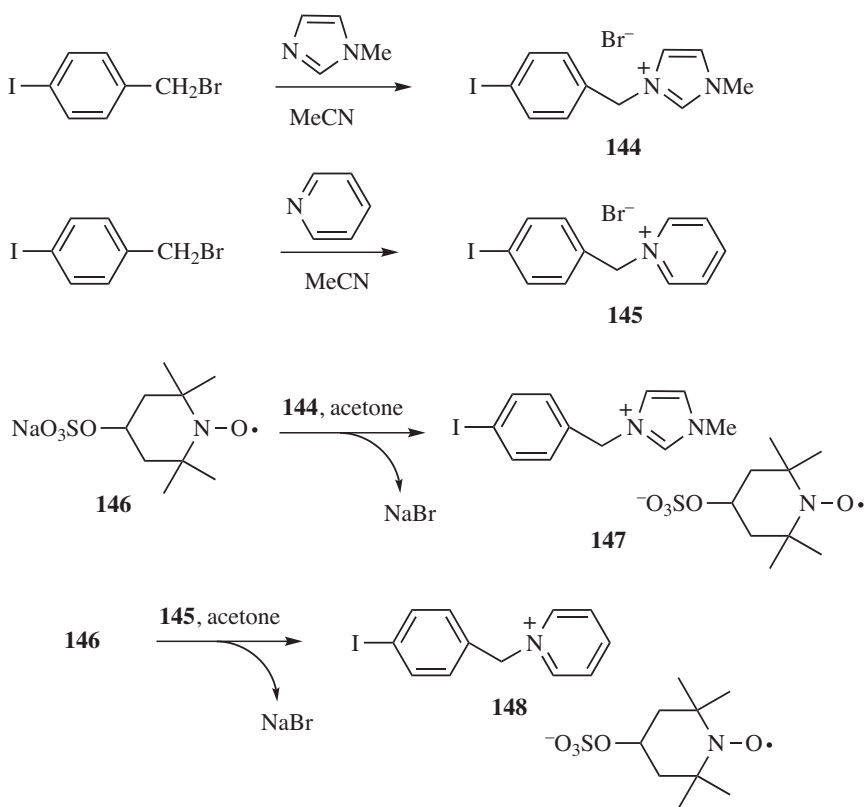
Scheme 5.43

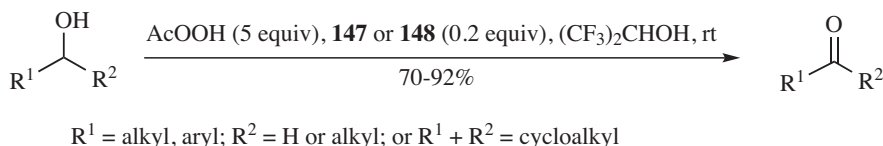
comparison, the ratio of catalytic iodine to ruthenium in the non-recyclable tandem catalytic system PhI/RuCl₃ was 31 : 1 (Section 4.3).

Bifunctional catalysts **142** and **143** can be used for environmentally benign oxidation of alcohols or alkylarenes at the benzylic position (Scheme 5.44) [114]. These reactions, using Oxone as stoichiometric oxidant, afford the corresponding carbonyl compounds (or carboxylic acids in the oxidations of benzyl alcohol or toluene) in high yields under mild conditions and convenient work-up. Both catalysts **142** and **143** show similar catalytic activity in the oxidation of alcohols, while catalyst **143** has noticeably higher catalytic reactivity in oxidation at the benzylic position. Furthermore, these SiO₂-supported bifunctional catalysts can be recovered by simple filtration and directly reused [114].

**Scheme 5.44**

Efficient recyclable bifunctional catalysts bearing ionic-liquid-supported TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) and iodoarene moieties have been developed and used for the environmentally benign catalytic oxidation of alcohols [115]. Ion-supported iodoarene–TEMPO bifunctional catalysts **147** and **148** were synthesized from ion-supported iodoarenes **144** and **145** by anionic exchange with TEMPO-sulfonate salt **146** (Scheme 5.45).

**Scheme 5.45**

**Scheme 5.46**

Ion-supported iodoarene–TEMPO bifunctional catalysts **147** and **148** have been employed as catalysts for the oxidation of alcohols to the corresponding carbonyl compounds using peracetic acid as a green and practical oxidant (Scheme 5.46). Furthermore, catalysts **147** and **148** could be conveniently recovered and reused without any loss of catalytic activity [115].

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