6

Reactions of Hypervalent Iodine Reagents in Green Solvents and under Solvent-Free Conditions

Typical reactions of common hypervalent iodine reagents are performed in non-recyclable organic solvents (dichloromethane, dimethyl sulfoxide, acetonitrile, etc.), which have potentially damaging environmental properties. The development of reactions using environmentally friendly solvents or solvent-free procedures is one of the active fields in organic synthesis due to a recent demand for realization of green chemical processes. The "greener" chemical syntheses in water or recyclable solvents, or under solvent-free procedures using mechanochemical mixing, microwave and ultrasound irradiation, have previously been summarized in two reviews [1, 2].

## 6.1 Reactions of Hypervalent Iodine Reagents in Water

The development of aqueous-phase reactions using environmentally friendly reagents is one of the active fields in organic synthesis [3–5]. Several protocols for reactions of hypervalent iodine reagents in water and environmentally-friendly aqueous solvent systems have been developed.

Iodosylbenzene, $(PhIO)_n$, in the presence of a hydroxylic solvent (water or alcohols) or an appropriate catalyst (Lewis acid, bromide or iodide anions, transition metal complex, etc.) can be effectively depolymerized, generating highly reactive monomeric species. Numerous examples of oxidations using iodosylbenzene in aqueous solutions have been reported. Moriarty and coworkers reported a series of oxidations of organic substrates with iodosylbenzene in hydroxylic solvents [6, 7]. For example, the oxidation of dihydropyran, cyclohexene and styrene with iodosylbenzene in aqueous solution leads predominantly to rearranged products [7]. Thus, the oxidation of dihydropyran (1) with iodosylbenzene in water affords tetrahydro-2-furaldehyde (2) via carbocationic ring contraction (Scheme 6.1) [7].

Kita, Tohma and coworkers have found that iodosylbenzene can be activated in aqueous solutions by addition of bromide salts to the reaction mixture [8, 9]. In particular, the oxidation of sulfides with iodosylbenzene in the presence of catalytic amounts of quaternary ammonium bromides selectively affords respective sulfoxides in high yields [8, 10]. The iodosylbenzene/KBr system in aqueous solution can be used for the

1   **2**

Scheme 6.1

R = Ph(CH$_2$)$_2$, BnO(CH$_2$)$_3$, EtO$_2$C(CH$_2$)$_4$, N$_3$(CH$_2$)$_4$, etc.
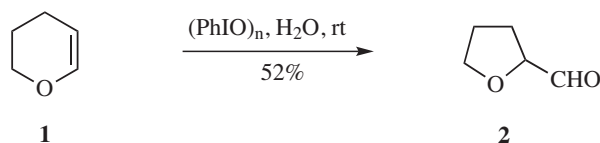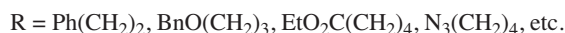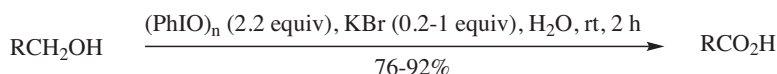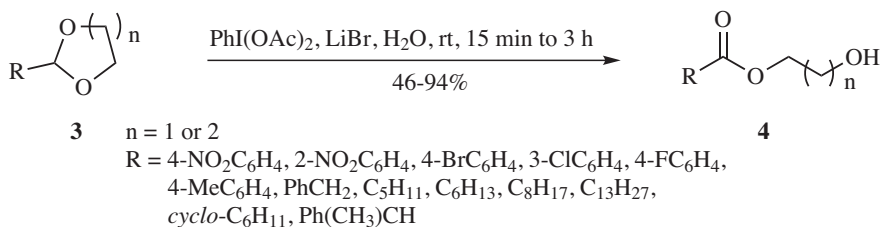
Scheme 6.2

oxidation of various primary and secondary alcohols, even in the presence of sensitive functional groups such as ether, ester, sulfonamide and azido groups. Primary alcohols under these conditions afford carboxylic acids (Scheme 6.2), while the oxidation of secondary alcohols under similar conditions furnishes ketones in almost quantitative yield [9, 11].

Activation of iodosylbenzene in the presence of KBr has been explained by the initial depolymerization of (PhIO)$_n$ with the formation of a highly reactive intermediate PhI(Br)O$^-$ K$^+$, which reacts with alcohols to yield the corresponding carbonyl compound with regeneration of KBr [11].
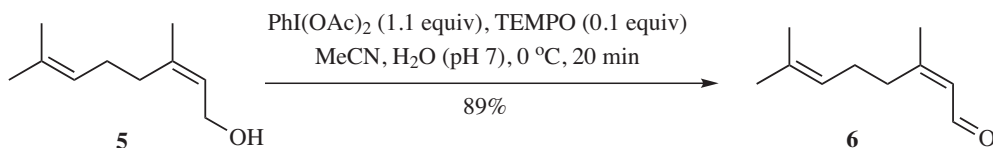
[Bis(acyloxy)iodo]arenes in the presence of bromide anion in water also oxidize primary and secondary alcohols similarly to the (PhIO)$_n$/KBr system [11,12]. The oxidation of primary alcohols using ArI(OAc)$_2$/KBr in water or aqueous methanol affords carboxylic acids or esters [9, 13], while the oxidation of secondary alcohols under similar conditions results in the formation of the respective ketones in excellent yields [14]. Aldehydes can be converted into methyl esters by a similar procedure using PhI(OAc)$_2$/NaBr in an acidic aqueous methanol solution [15]. Likewise, acetals **3** can be converted into the corresponding hydroxyalkyl carboxylic esters **4** by oxidation with PhI(OAc)$_2$/LiBr in water (Scheme 6.3) [16].

The oxidation of alcohols with (diacetoxyiodo)benzene in the presence of catalytic amounts of TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) in aqueous solutions is a common synthetic procedure (Section 3.1.5) [17–23]. An optimized protocol, published in *Organic Synthesis* for the oxidation of nerol **5** to nepal **6** (Scheme 6.4), consists of the treatment of the alcohol **5** solution in buffered (pH 7) aqueous acetonitrile with (diacetoxyiodo)benzene and TEMPO (0.1 equivalent) at 0 °C for 20 min [17].
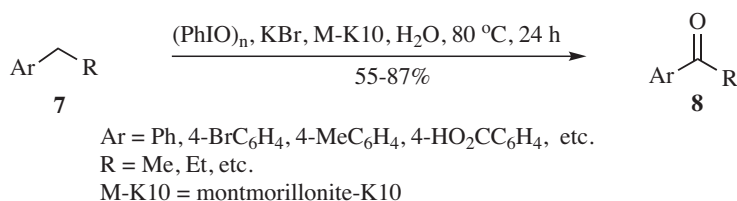
Various organic substrates **7** with a benzylic C–H bond can be effectively oxidized to aryl ketones **8** by iodosylbenzene in the presence of KBr and montmorillonite-K10 (M-K10) clay in water (Scheme 6.5) [24].

3   n = 1 or 2   **4**
         R = 4-NO$_2$C$_6$H$_4$, 2-NO$_2$C$_6$H$_4$, 4-BrC$_6$H$_4$, 3-ClC$_6$H$_4$, 4-FC$_6$H$_4$,
            4-MeC$_6$H$_4$, PhCH$_2$, C$_5$H$_{11}$, C$_6$H$_{13}$, C$_8$H$_{17}$, C$_{13}$H$_{27}$,
            cyclo-C$_6$H$_{11}$, Ph(CH$_3$)CH

Scheme 6.3

Scheme 6.4

Ar = Ph, 4-BrC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-HO$_2$CC$_6$H$_4$, etc.
R = Me, Et, etc.
M-K10 = montmorillonite-K10

Scheme 6.5

9   R = Cl, NO$_2$, MeO, CF$_3$, etc.   10
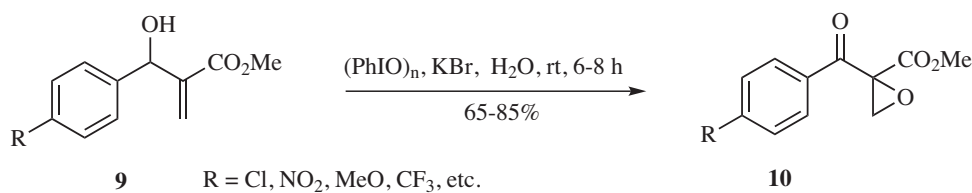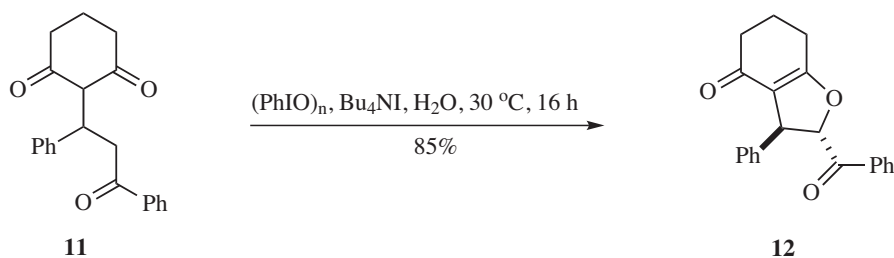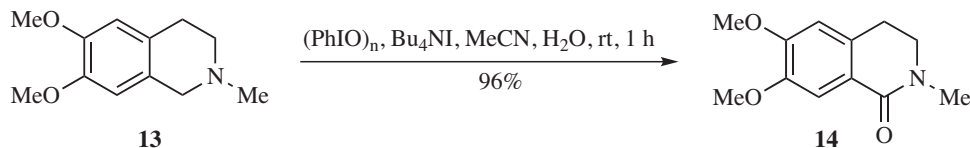
Scheme 6.6

Treatment of Baylis–Hillman adducts **9** with iodosylbenzene in the presence of catalytic KBr in water at room temperature affords the corresponding acyloxiranes **10** in good yields (Scheme 6.6) [25].

An efficient aqueous oxidative cyclization of Michael adducts (e.g., compound **11,** Scheme 6.7) promoted by the combination of iodosylbenzene with tetrabutylammonium iodide provides a convenient route to functionalized fused dihydrofuran derivatives (e.g., product **12**) in moderate to excellent yields with high diastereoselectivities [26].
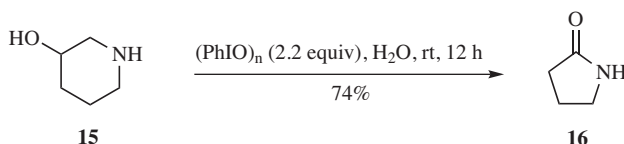
The oxidation of *N*-methyltetrahydroisoquinolines (e.g., **13**) with iodosylbenzene in the presence of a catalytic amount of tetrabutylammonium iodide in aqueous solvents affords the respective lactams (e.g., **14**) in almost quantitative yields, as exemplified in Scheme 6.8 [27].

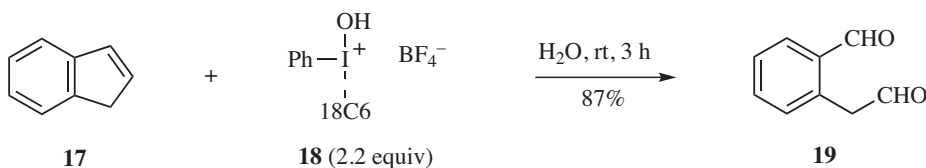*Scheme 6.7*

Scheme 6.8

Scheme 6.9

The oxidation of 3-hydroxypiperidine (**15**) with iodosylbenzene in water affords 2-pyrrolidinone **16** directly in good yield (Scheme 6.9) [28]. The mechanism of this reaction probably involves oxidative Grob fragmentation yielding an imino aldehyde, which upon hydrolysis affords 2-pyrrolidinone by a cyclization–oxidation sequence [28]. The oxidative cyclization of aldoximes using iodosylbenzene in neutral aqueous media in the presence of surfactants has been employed in the synthesis of functionalized isoxazolines [29].

Ochiai and coworkers have reported several useful oxidations employing the activated iodosylbenzene species in aqueous solution [30–34]. The monomeric iodosylbenzene complex **18** in the presence of water can cleave the carbon–carbon double bond of indene **17** to form dialdehyde **19** (Scheme 6.10) [30]. Similar oxidative cleavage of various alkenes can be performed by using iodosylbenzene in water in the presence of HBF$_4$. This convenient procedure provides a safe alternative to the ozonolysis of alkenes [30].

The oligomeric iodosylbenzene sulfate **20** is a readily available, stable and water-soluble reagent with a reactivity pattern similar to that of activated iodosylbenzene [35–40]. It reacts with alkenes, alcohols and aryl alkyl sulfides in aqueous acetonitrile at room temperature to afford the respective products of oxidation **21**–**24** in good yields (Scheme 6.11) [35, 36].

Zhu and Wei have reported a mild and highly efficient procedure for the oxidation of alcohols to the corresponding aldehydes or ketones using oligomeric iodosylbenzene sulfate **20** in water in the presence of β-cyclodextrin, which serves as a biomimetic catalyst. The oxidation proceeded in water to afford aldehydes or ketones in excellent yields and high selectivity without overoxidation to carboxylic acids [41].

Kita and coworkers have developed a method for preparing *p*-quinone derivatives from phenol ether derivatives using [bis(trifluoroacetoxy)iodo]benzene in water. This reaction proceeds in high yields under mild reaction conditions [42]. μ-Oxo-bridged hypervalent iodine trifluoroacetate **26** is a particularly effective reagent for oxidations in aqueous solutions. Reagent **26** is generally more reactive than PhI(O$_2$CCF$_3$)$_2$,
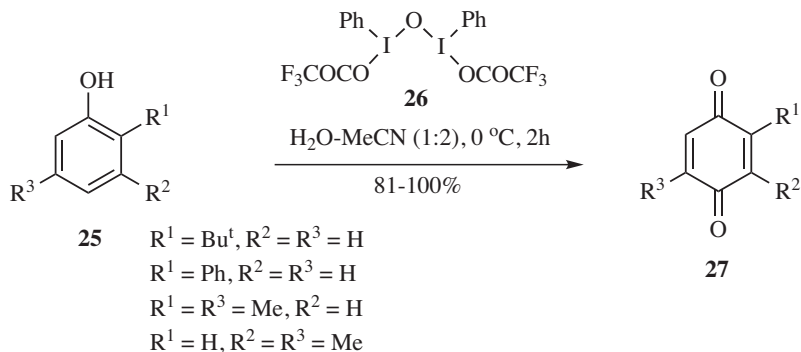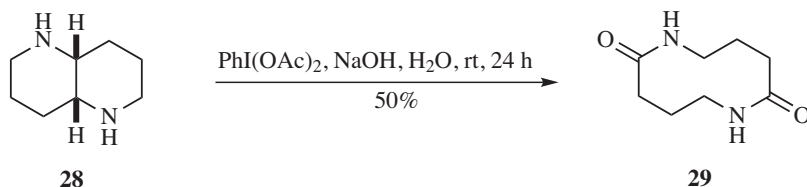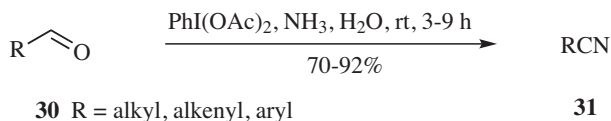

Scheme 6.10
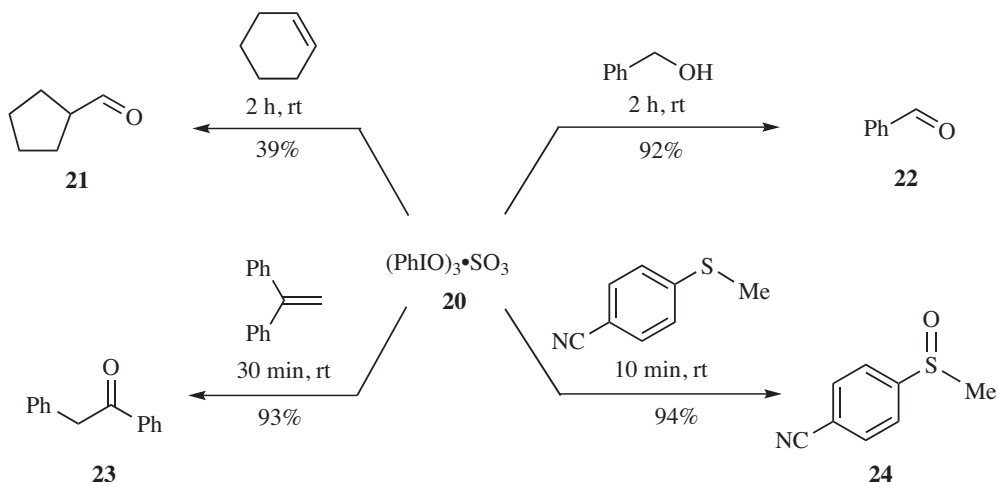
Scheme 6.11

especially toward phenolic substrates. In a specific example, μ-oxo-bridged trifluoroacetate **26** in aqueous media converts phenols **25** into the dearomatized quinones **27** in excellent yields (Scheme 6.12) [43].

Kozlowski and coworkers have reported an oxidative rearrangement of *cis-* and *trans-*1,5-diazadecalins promoted by (diacetoxyiodo)benzene in aqueous solution. In a specific example, upon treatment with (diacetoxyiodo)benzene in aqueous NaOH, 1,5-diaza-*cis*-decalin (**28**) undergoes oxidation along with fragmentation to yield the ring-expanded bislactam **29** (Scheme 6.13) [44].

A mild and high yielding protocol has been reported for the transformation of aldehydes **30** into nitriles **31** using (diacetoxyiodo)benzene in aqueous ammonia under mild reaction conditions at room temperature (Scheme 6.14) [45].

Several oxidations with iodine(V) reagents in aqueous solutions have been reported in the literature. Kuhakarn and coworkers have found that IBX can be used for the oxidation of alcohols in a water/dichloromethane (1 : 10) mixture in the presence of tetrabutylammonium bromide [46]. Vinod and coworkers have developed water-soluble analogs of IBX, *m*-iodoxyphthalic acid (mIBX) **32** [47] and a similar derivative of terephthalic acid **33** (Figure 6.1) [48], which can oxidize benzylic and allylic alcohols to


Scheme 6.12

Scheme 6.13

30 R = alkyl, alkenyl, aryl

Scheme 6.14

carbonyl compounds in water. Zhang and coworkers have prepared the IBX derivatives **34** and **35** bearing a trimethylammonium group, which possess excellent solubility in water [49]. The structure of compound **34** was established by single-crystal X-ray diffraction analysis. Compound **34** is a useful reagent for the oxidation of various β-keto esters to the corresponding dehydrogenated products in aqueous solution [49].

6.2   Reactions of Hypervalent Iodine Reagents in Recyclable Organic Solvents

Ionic liquids have gained recognition as environmentally benign alternatives to the more volatile organic solvents [50,51]. Ionic liquids possess many attractive properties, such as wide liquid range, negligible vapor pressure, high thermal stability, good solvating ability for a wide range of substrates, easy recoverability and
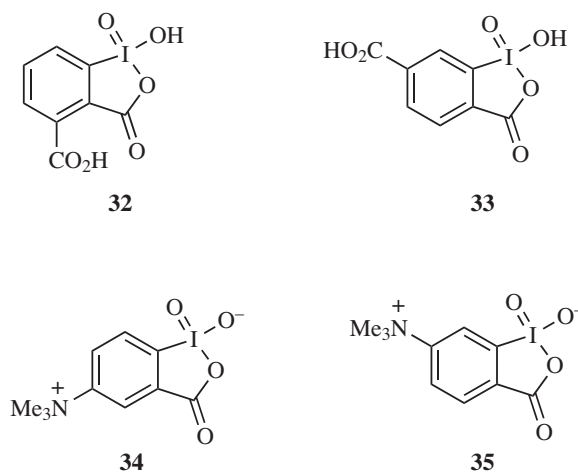
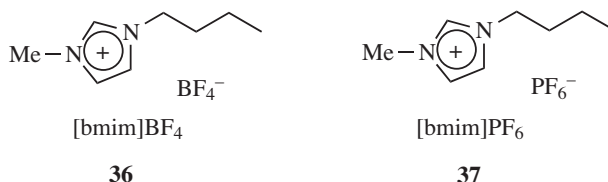**Figure 6.1**   *Water-soluble analogs of 2-iodoxybenzoic acid (IBX).*

Figure 6.2   *Structures of hydrophilic [bmim]BF4 (**36**) and hydrophobic [bmim]PF6 (**37**) ionic liquids.*

reusability. Their nonvolatile nature can reduce the emission of toxic organic compounds and facilitate the separation of products and/or catalysts from the reaction solvents.

The use of ion-supported [bis(acyloxy)iodo]arene in the ionic liquid $[emim]^+[BF_4]^-$ (1-ethyl-3-methylimidazolium tetrafluoroborate) in the presence of bromide anion or ion-supported TEMPO for the oxidation of primary and secondary alcohols is discussed in Section 5.3.3 [52, 53].

Several research groups have used ionic liquids for the oxidation of alcohols with *o*-iodoxybenzoic acid (IBX) or Dess–Martin periodinane (DMP). Alcohols undergo smooth oxidation with IBX or with DMP in hydrophilic [bmim]BF$_4$ (structure **36,** Figure 6.2) and hydrophobic [bmim]PF$_6$ (structure **37**) ionic liquids at room temperature under mild conditions to afford the corresponding carbonyl compounds in excellent yields with high selectivity [54]. Similar results were obtained for the oxidation of alcohols with IBX and DMP using ionic liquid [bmim]Cl (1-butyl-3-methylimidazolium chloride) [55, 56]. IBX- and DMP-promoted oxidations are faster in ionic liquids compared to conventional solvents such as DMSO, DMF, ethyl acetate and water. Recovery of the by-product iodosobenzoic acid is especially simple in ionic liquids. The recovered ionic liquids can be recycled in subsequent reactions with consistent activity.

IBX in the ionic liquid [bmim]Br was found to be an efficient and eco-friendly reagent for the oxidation of 17α-methylandrostan-3β,17β-diol (**38**) to mestanolone (**39**) in good yield (Scheme 6.15) [57]. The product is easily separated from the reaction mixture by extraction with diethyl ether.

An ionic liquid of a different type (*n*-butylpyridinium tetrafluoroborate, [BPy]BF$_4$) has been used as a recyclable solvent for the reaction of 4-benzoylbutyric acids **40** with [hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]benzene (HDNIB) leading to 5-benzoyldihydro-2(3*H*)-furanones **41** (Scheme 6.16) [58].

A different recyclable solvent, PEG-400 [poly(ethylene glycol-400)], has been used in the one-pot synthesis of 2-arylimidazo[1, 2-*a*]pyrimidines by the reaction of ketones with HDNIB and 2-aminopyrimidine. Significant rate enhancements and improved yields have been observed when compared with regular organic solvents [59].

Scheme 6.15

Ar = Ph, 4-MeC$_6$H$_5$, 4-MeOC$_6$H$_5$, 4-ClC$_6$H$_5$, 4-BrC$_6$H$_5$, etc.
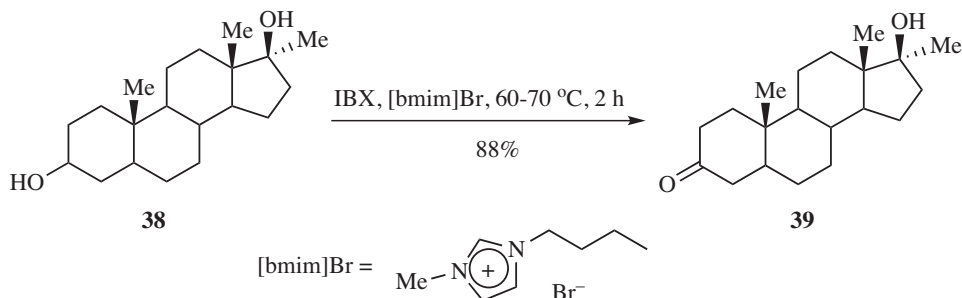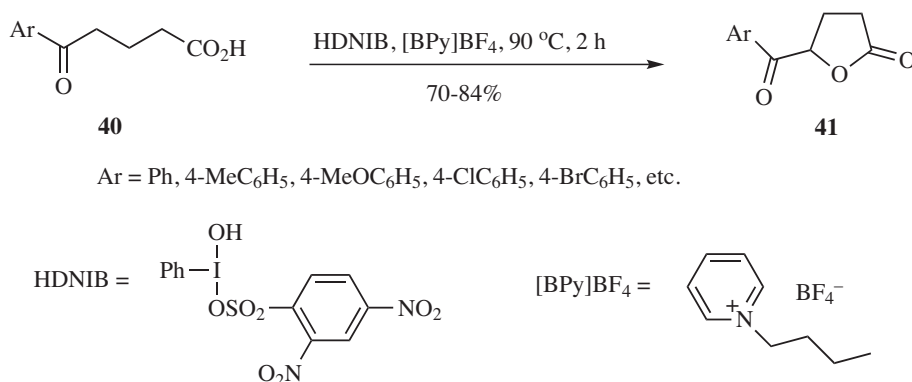
Scheme 6.16

6.3   Reactions of Hypervalent Iodine Reagents under Solvent-Free Conditions
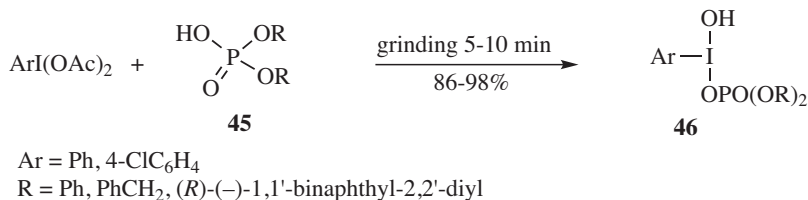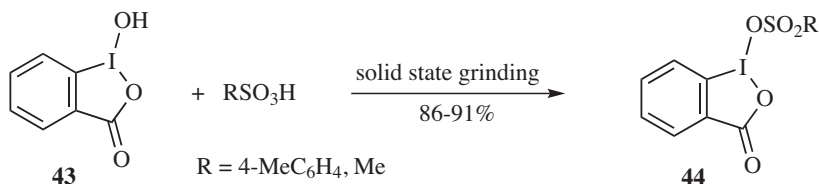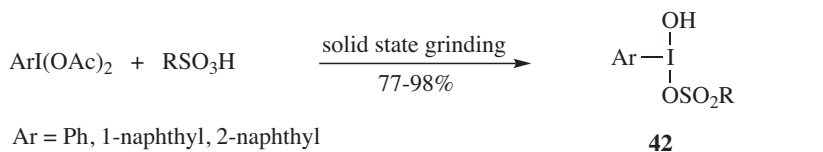
Solvent-free reactions have many advantages such as reduced pollution, lower costs and the simplicity of the processes involved [60]. The solvent-free preparation of several important hypervalent iodine reagents has been reported [61, 62]. [Hydroxy(sulfonyloxy)iodo]arenes (**42**) have been prepared in excellent yields by the solid-state reaction simply by grinding (diacetoxyiodo)arenes and appropriate sulfonic acids for several minutes in an agate mortar [61]. Tosyloxy- and mesyloxy benziodoxoles **44** can be prepared by a similar solvent-free procedure starting from 2-iodosylbenzoic acid (**43**) [61]. Likewise, [hydroxy(phosphoryloxy)iodo]arenes **46** have been conveniently prepared by a solvent-free method from (diacetoxyiodo)arenes and phosphate esters **45** (Scheme 6.17) [62].
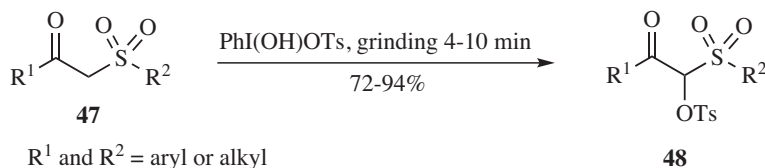
Several examples of solvent-free reactions of hypervalent iodine reagents have been reported in the literature [61, 63–67]. Tosyloxylation of ketones or 1,3-diketones using [hydroxy(tosyloxy)iodo]benzene (HTIB) under solvent-free conditions takes place in a few minutes to give the respective α-tosyloxycarbonyl compounds in reasonable yields [61]. Likewise, α-tosyloxy β-keto sulfones **48** can be prepared under solvent-less conditions at room temperature (Scheme 6.18) [63]. This simple procedure consists of grinding together a neat mixture of β-keto sulfone **47** and HTIB at room temperature using a pestle and mortar; the reaction is complete in 4–10 min, giving products **48** in high yields [63].

A series of unsaturated compounds **49,** including α,β-unsaturated ketones, cinnamates, cinnamides and styrenes, have been aminobrominated to give products **50** with good yields and excellent diastereoselectivities under mechanical milling conditions, using TsNH$_2$ and *N*-bromosuccinimide (NBS) as the nitrogen and bromine sources, promoted by (diacetoxyiodo)benzene (Scheme 6.19) [64].

Solvent-free conditions are particularly useful for the hypervalent iodine mediated syntheses of heterocycles. An efficient and environmentally benign one-pot synthesis of 2-aryl/heteroaryl-benzothiazoles by the reaction of 2-aminothiophenol and aryl/heteroaryl aldehydes mediated by hypervalent iodine(III) reagents under solvent-free condition at room temperature has been developed [65]. These reactions are carried out by grinding the reactants with PhI(O$_2$CCF$_3$)$_2$ or PhI(OAc)$_2$ in a mortar with pestle. The advantages of this protocol are the one-step procedure, mild reaction conditions, high yields of the products and no side reactions [65]. Likewise, the oxidative cyclization of 2-pyridyl- and 2-quinolyl-hydrazones with PhI(O$_2$CCF$_3$)$_2$ or PhI(OAc)$_2$ to the corresponding 3-aryl[1,2,4]triazolo[4,3-*a*]pyridines and 1-aryl[1,2,4]triazolo[4,3-*a*]quinolines has been performed under solvent-free conditions by grinding the reaction components [66]. The application of a solvent-free procedure for the synthesis of various 2-arylbenzimidazoles **53** from *o*-phenylenediamine (**51**) and aldehydes **52** in the presence of hypervalent iodine as the oxidant is illustrated by Scheme 6.20 [67].

ArI(OAc)$_2$ + RSO$_3$H $\xrightarrow[\text{77-98\%}]{\text{solid state grinding}}$ Ar$-$I (OH, OSO$_2$R)

42

Ar = Ph, 1-naphthyl, 2-naphthyl
R = 4-MeC$_6$H$_4$, Me, (1*R*)-10-camphoryl

43 + RSO$_3$H $\xrightarrow[\text{86-91\%}]{\text{solid state grinding}}$ **44**

R = 4-MeC$_6$H$_4$, Me

ArI(OAc)$_2$ + **45** (HO,OR–P(=O)–OR) $\xrightarrow[\text{86-98\%}]{\text{grinding 5-10 min}}$ Ar$-$I (OH, OPO(OR)$_2$)

46

Ar = Ph, 4-ClC$_6$H$_4$
R = Ph, PhCH$_2$, (*R*)-(–)-1,1'-binaphthyl-2,2'-diyl

Scheme 6.17

R^{1}C(O)CH$_2$S(O)$_2$R^2 **47** $\xrightarrow[\text{72-94\%}]{\text{PhI(OH)OTs, grinding 4-10 min}}$ R^{1}C(O)CH(OTs)S(O)$_2$R^2 **48**

R^1 and R^2 = aryl or alkyl

Scheme 6.18

R^{1}CH=CHC(O)R^2 **49** + TsNH$_2$ + NBS $\xrightarrow[\text{52-83\%}]{\text{PhI(OAc)}_2, \text{ ball milling (30 Hz), rt}}$ R^{1}CH(Br)CH(NHTs)C(O)R^2 **50**

R^1 and R^2 = aryl or alkyl

Scheme 6.19

51 (benzene-1,2-diamine, NH$_2$/NH$_2$) + **52** (ArC(O)H) $\xrightarrow[\text{83-94\%}]{\substack{\text{PhI(OAc)}_2, \text{ rt, 3-5 min} \\ \text{solvent-free stirring}}}$ **53** (2-aryl benzimidazole)

Ar = Ph, 4-ClC$_6$H$_4$, 2-ClC$_6$H$_4$, 4-EtC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-MeOC$_6$H$_4$,
4-BrC$_6$H$_4$, 4-FC$_6$H$_4$, 4-Bu^{t}C$_6$H$_4$, 2-MeC$_6$H$_4$, 2-furyl, 2-thienyl,
2-pyrrolyl, 2-pyridinyl

Scheme 6.20
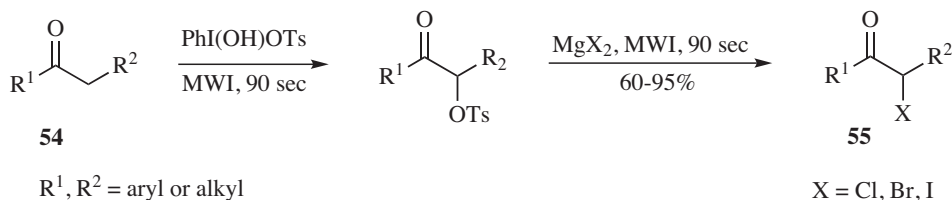
Scheme 6.21

Several examples of solvent-free reactions of hypervalent iodine reagents under microwave irradiation conditions have been reported [2, 68–72]. A solvent-less oxidation of 1,4-dihydropyridines to the respective pyridines can be performed using [bis(trifluoroacetoxy)iodo]benzene at room temperature under microwave irradiation conditions [68]. Carbonyl compounds (aldehydes, ketones and esters) can be converted into the respective α-[(2,4-dinitrobenzene)sulfonyl]oxy carbonyl compounds by the reaction of the neat carbonyl compounds with [hydroxy(2,4-dinitrobenzenesulfonyloxy)iodo]benzene (HDNIB) under microwave irradiation in less than 40 s [69]. Likewise, α-halocarbonyl compounds **55** can be conveniently prepared by sequential treatment of carbonyl compounds **54** with [hydroxy(tosyloxy)iodo]benzene followed by magnesium halides under solvent-free microwave irradiation (MWI) conditions (Scheme 6.21) [70].

Several examples of microwave-promoted reactions of hypervalent iodine reagents in organic solvents, such as methanol [73], chloroform [73], DMF [74] and THF [75], have also been reported.

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