# Preparation and Reactivity of Polystyrene-Supported Iodosylbenzene: Convenient Recyclable Oxidizing Reagent and Catalyst

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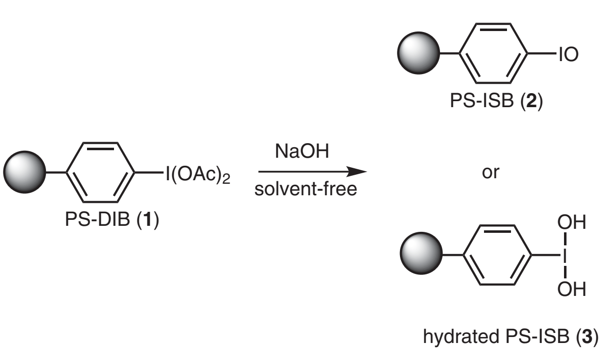
**Abstract:** A facile preparation of novel polystyrene-supported iodosylbenzene (PS-ISB, loading of IO up to 1.50 mmol/g) from iodopolystyrene is described. This resin has been successfully used for efficient oxidation of a diverse collection of alcohols to aldehydes and ketones in the presence of $BF_3{\cdot}OEt_2$. PS-ISB can also be employed as efficient co-catalyst in combination with $RuCl_3$ in the catalytic oxidation of alcohols and aromatic hydrocarbons, respectively, to corresponding carboxylic acids and ketones using Oxone as the stoichiometric oxidant.

**Key words:** polymers, iodine, oxidation, iodosylbenzene, recyclable reagent

In recent years, hypervalent iodine compounds have been widely used in organic synthesis for various synthetically useful oxidative transformations with many advantages, like mild reaction conditions, simple workup, and the environmentally benign nature of the reagents.[1] Iodosylbenzene, $(PhIO)_n$, is particularly important as an oxygen-transfer agent that has found widespread application in catalytic oxygenation reactions after the discovery of its supreme efficacy as a source of oxygen atoms for oxidations catalyzed by cytochrome P-450 and by discrete transition-metal complexes.[2,3] However, stoichiometric amount of iodobenzene as a waste product is produced in these reactions, which leads to low atom economy and complicated isolation and purification of the products. Furthermore, the practical use of iodosylbenzene is hampered by its low stability and potentially explosive properties upon moderate heating and insolubility in most solvents as a result of its polymeric structure, $(PhIO)_n$.[3,4]

Polymer-supported hypervalent iodine reagents, however, overcome these drawbacks and have the similar reactivities as their monomeric analogues.[5] Several polystyrene-supported hypervalent reagents previously reported by our group, such as polystyrene-supported (diacetoxyiodo)benzene (PS-DIB),[6a] poly{[4-(hydroxy)(tosyloxy)iodo]styrene} (PS-HTIB),[6b] polystyrene-supported phenyliodine(III)bis(trifluoroacetate) (PS-PIFA),[6c] polystyrene-supported iodosylbenzene sulfate (PS-IBS),[6d] are employed as efficient oxidants, polystyrene-supported (dichloroiodo)benzene (PS-DCIB)[6e] as chlorination and oxidation reagents, and polystyrene-supported alkenyl(phenyl) iodonium salts[6f] as synthons of alkenyl cations. The reduced form of these reagents, iodopolystyrene (PS-IB), can be conveniently recovered from reaction mixtures and reused for the preparation of the reagent.

Despite significant interest in polymer-supported hypervalent iodine reagents and the importance of iodosylarenes in organic chemistry, the polystyrene-supported variant of iodosylbenzene (PS-ISB) has not been reported in the literature. Our initial attempts to prepare PS-ISB by a standard approach involving treatment of respective (diacetoxyiodo)arene, PS-DIB, with the aqueous solution of NaOH were unsuccessful. We have found, however, that PS-DIB (**1**)[6a,7] can be effectively converted into PS-ISB (**2**) under solvent-free conditions (Scheme 1).[8] A similar solvent-free methodology has previously been used for the preparation of [hydroxy(tosyloxy)iodo]benzene[9a] and oligomeric iodosylbenzene sulfate.[9b]



**Scheme 1** Preparation of polystyrene-supported iodosylbenzene

In a typical procedure PS-DIB (**1**) and sodium hydroxide were ground intensively in a mortar at room temperature for 10 minutes. The resulting mixture was left to stay at room temperature for 2 hours, and then water was added and stirred overnight, then washed subsequently with water, acetone, and diethyl ether, and dried in vacuum to obtain a brownish-yellow powder. The loading of IO was 1.50 mmol $g^{-1}$ (determined by titration of the iodine liberated from a solution of KI). The IR spectra of the resin have a typical peak at 760 $cm^{-1}$ (I=O), which is similar to that of $(PhIO)_n$. And the disappearance of peaks at 1564 and 1288 $cm^{-1}$ [the characteristic peaks of PS-DIB (**1**)] in-

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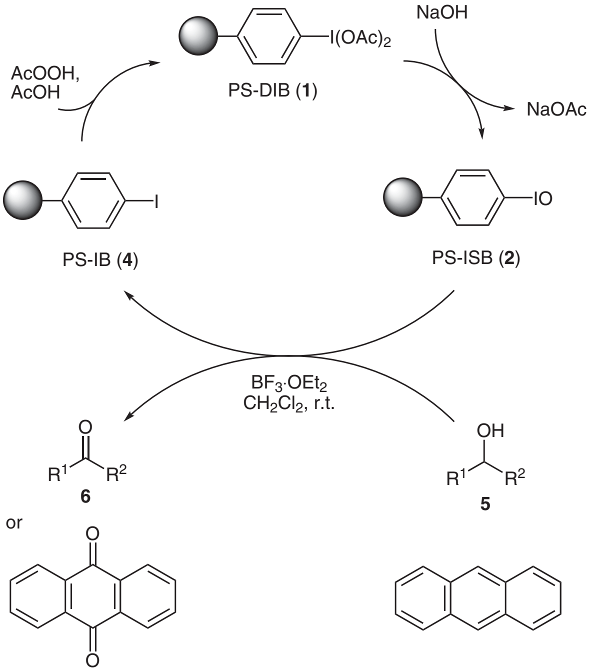
dicates that nearly all of $I(OAc)_2$ groups are converted into the IO groups. However, based on the elemental analysis of PS-ISB (**2**) samples on oxygen and iodine, the ratio of O/I is about 1.85 which is much higher than the calculated value of 1:1. It is likely that the IO groups in PS-IBS are partially hydrated as illustrated by structure **3** (Scheme 1).

The oxidative properties of PS-ISB were initially evaluated in the reaction with various alcohols **5** (Scheme 2).[10] The results of oxidations are summarized in Table 1. As expected, reactivity of PS-ISB in the $BF_3{\cdot}OEt_2$-catalyzed oxidation of alcohols is similar to $(PhIO)_n$, and the polymer-supported reagent **2** can be used for efficient oxidation of various alcohols **5** to the corresponding carbonyl compounds **6** under mild conditions. Benzylic alcohols are oxidized to the corresponding aldehydes with 100% conversion after 1.5–12 hours except 4-methoxylbenzyl alcohol (Table 1, entries 1–4). The highly reactive 4-methoxylbenzyl alcohol under these conditions gave a dark complex mixture of products (Table 1, entry 5); however, 4-methoxy-benzaldehyde was obtained smoothly in the absence of $BF_3{\cdot}OEt_2$ (Table 1, entry 6). Reactions of all other substrates with PS-ISB in the absence of $BF_3{\cdot}OEt_2$ were extremely slow and did not afford any measurable yield of product even after 12 hours. Primary aliphatic alcohol, 1-octanol (Table 1, entry 7) was converted into a complex mixture, and secondary alcohols (Table 1, entries 8–13) were selectively oxidized to the respective ketones in good yields.

The PS-ISB/$BF_3{\cdot}OEt_2$ system can also be used for the oxidation at phosphorus atom, as illustrated by the conversion of triphenylphosphine into triphenylphosphine oxide in excellent yield (Table 1, entry 16). Interestingly, the PS-ISB/$BF_3{\cdot}OEt_2$ system can oxidize anthracene to anthraquinone in good yield (Table 1, entry 14), while in the absence of $BF_3{\cdot}OEt_2$, using catalytic amount of binuclear iron(III) phthalocyanine(μ-oxodimer),[11] anthracene can be oxidized only in low yield (8–9%) after long time (72 h, entry 15).

The final products of all oxidations can be conveniently separated from byproduct PS-IB (**4**) by simple filtration and isolated in good purity after evaporation of solvent. The recycled PS-ISB does not show significant loss of activity in oxidation of 4-nitrobenzyl alcohol to 4-nitrobenzaldehyde (Table 1, entry 3).



**Scheme 2** Oxidation of organic substrates using PS-ISB (**2**) as a recyclable reagent

**Table 1** Oxidation of Organic Substrates Using Polystyrene-Supported Iodosylbenzene[a]

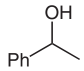
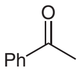
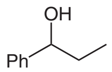
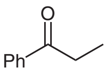
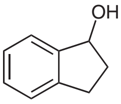
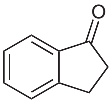
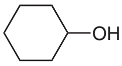
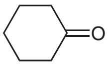
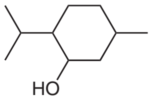
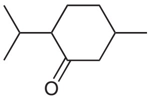
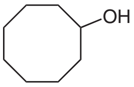
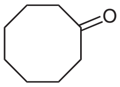
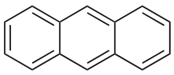
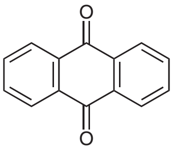
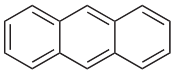
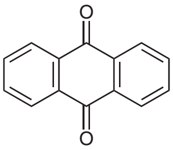
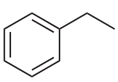
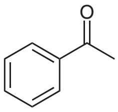
| Entry | Substrate | $BF_3{\cdot}OEt_2$ (equiv) | Product | Time (h) | Conversion (%)[b] | Yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | BnOH | 1.5[d] | PhCHO | 12 | >95 | 80[e] |
| 2 | $4\text{-}O_2NC_6H_4CH_2OH$ | 1.5 | $4\text{-}O_2NC_6H_4CHO$ | 1.5 | >95 | 85 |
| 3 | $4\text{-}O_2NC_6H_4CH_2OH$ | 1.5 | $4\text{-}O_2NC_6H_4CHO$ | 1.5 | >95 | 83[f] |
| 4 | $3\text{-}O_2NC_6H_4CH_2OH$ | 1.5 | $3\text{-}O_2NC_6H_4CHO$ | 12 | >99 | 78 |
| 5 | $4\text{-}MeOC_6H_4CH_2OH$ | 1.5 | $4\text{-}MeOC_6H_4CHO$ | 0.25 | >99 | –[g] |
| 6 | $4\text{-}MeOC_6H_4CH_2OH$ | none | $4\text{-}MeOC_6H_4CHO$ | 6 | >99 | 76 |
| 7 | $n\text{-}C_8H_{17}OH$ | 1.5 | $n\text{-}C_7H_{15}CHO$ | 24 | >99 | –[g] |
| 8 |  | 1.5 |  | 12 | 99 | 80 |
| 9 |  | 1.5 |  | 12 | >99 | 88[e] |

**Table 1** Oxidation of Organic Substrates Using Polystyrene-Supported Iodosylbenzene[a] (continued)

| Entry | Substrate | $BF_3·OEt_2$ (equiv) | Product | Time (h) | Conversion (%)[b] | Yield (%)[c] |
|---|---|---|---|---|---|---|
| 10 |  | 1.5 |  | 12 | >99 | 85 |
| 11 |  | 1.5 |  | 12 | 95 | 66 |
| 12 |  | 1.5 |  | 12 | 90 | 70[e] |
| 13 |  | 1.5 |  | 12 | 99 | 85 |
| 14 |  | 3.0 |  | 3 | 99 | 67 |
| 15 |  | 0[h] |  | 72 | <10 | 0[i] |
| 16 | $Ph_3P$ | 1.5 | $Ph_3P=O$ | 12 | 99 | 92 |
| 17 |  | 1.5 |  | 48 | 0 | 0[i] |

[a] All reactions of organic substrate (0.2 mmol) were performed at r.t. in the presence of $BF_3·OEt_2$ and PS-ISB (1.5 equiv) in dry $CH_2Cl_2$ (2 mL).

[b] Based on disappearance of starting substrate measured by GC-MS.

[c] Yields of isolated products.

[d] In the absence of $BF_3·OEt_2$ this reaction is extremely slow and does not afford any measurable yield of product even after 12 h.

[e] Isolated as 2,4-dinitrophenylhydrazone.

[f] Regenerated PS-ISB (**2**) was used.

[g] Complex mixture was obtained.

[h] 5 mol% of binuclear iron(III) phthalocyanine(μ-oxodimer)[11] catalyst was added.

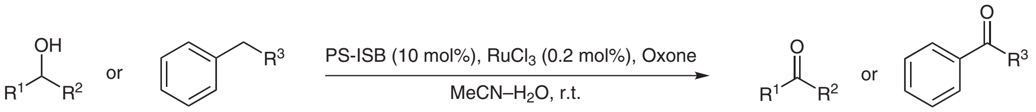
[i] The starting material was recovered.

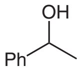
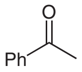
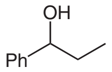
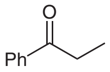
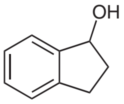
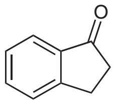
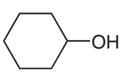
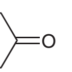
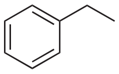
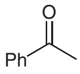
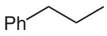
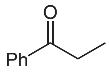
Considering active current research activity toward the development of catalytic systems based on hypervalent iodine chemistry,[1j,k,1o–q,1t,w] it would be interesting to test these oxidations (Scheme 2) using catalytic amount of PS-ISB. Recently, we have reported an extremely mild and efficient tandem catalytic system for the oxidation of alcohols and hydrocarbons based on a Ru(III)-catalyzed reoxidation of ArIO to $ArIO_2$ using Oxone as a stoichiometric oxidant.[12] Since the reactivity of polymer-supported hypervalent iodine reagents is generally similar to the monomeric analogues, we expected that PS-ISB (**2**) can serve as an active co-catalyst with Ru(III) species in the tandem catalytic system PS-ISB/$RuCl_3$. The results of the oxidation of some organic substrates using catalytic system PS-ISB/$RuCl_3$ and Oxone as a stoichiometric oxidant are summarized in Table 2. A special control experiment has shown that only traces of oxidation products (acids and ketones) are observed in these reactions in the absence of $RuCl_3$.

As expected, a variety of alcohols were smoothly oxidized to afford the respective oxidation products in good yields at room temperature.[13] Similar to the PhI/$RuCl_3$/Oxone procedure,[12] our protocol afforded carboxylic acids from primary alcohols (Table 2, entries 1–5) and ketones from the secondary alcohols (Table 2, entries 6–9). We also investigated the oxidation of C–H bonds by using the PS-ISB/$RuCl_3$ tandem catalytic system. Ethylbenzene shows good reactivity in conversion into acetophenone (Table 2, entry 10), while propylbenzene is less reactive (Table 2, entry 11).

Comparing the results of the two protocols (Table 1 and Table 2) we found that primary alcohols were oxidized to aldehydes in the PS-ISB/$BF_3·OEt_2$ system, while carboxylic acids were obtained in the tandem catalytic system

**Table 2** Oxidation of Organic Substrates Using Polystyrene-Supported Iodosylbenzene[a]



| Entry | Substrate | PS-catalyst | Oxone (equiv) | Product | Time (h) | Conversion (%)[b] | Yield (%)[c] |
|---|---|---|---|---|---|---|---|
| 1 | BnOH | PS-ISB | 3.0 | PhCOOH | 12 | 99 | 95 |
| 2 | BnOH | PS-ISB | 3.0 | PhCOOH | 24 | 99 | 93[d] |
| 3 | 3-$O_2NC_6H_4CH_2OH$ | PS-ISB | 3.0 | 3-$O_2NC_6H_4COOH$ | 12 | 99 | 95 |
| 4 | 4-$O_2NC_6H_4CH_2OH$ | PS-ISB | 3.0 | 4-$O_2NC_6H_4COOH$ | 12 | 99 | 90 |
| 5 | 4-$MeOC_6H_4CH_2OH$ | PS-ISB | 3.0 | 4-$MeOC_6H_4COOH$ | 24 | 99 | 60 |
| 6 |  | PS-ISB | 1.5 |  | 1.5 | 99 | 82 |
| 7 |  | PS-ISB | 1.5 |  | 4 | 99 | 84[e] |
| 8 |  | PS-ISB | 1.5 |  | 3.5 | 99 | 85[e] |
| 9 |  | PS-ISB | 1.5 |  | 6 | 99 | 70 |
| 10 |  | PS-ISB | 3.0 |  | 15 | 99 | 84 |
| 11 |  | PS-ISB | 6.1 |  | 24 | 60 | 35[e,f] |

[a] All reactions of organic substrate (0.2 mmol) were performed at r.t. in the presence of $RuCl_3$ (0.02 equiv), PS-ISB (0.1 equiv), and Oxone in MeCN–$H_2O$ (1:1, v/v, 2 mL).

[b] Based on disappearance of starting substrate measured by GC-MS.

[c] Yields of isolated products.

[d] Regenerated PS-ISB (**2**) was used.

[e] Isolated as 2,4-dinitrophenylhydrazone.

[f] Reaction mixture also contains 40% of unreacted propylbenzene.

PS-ISB/$RuCl_3$, because the initially formed aldehydes were subsequently oxidized by Oxone; secondary alcohols were oxidized to ketones in both protocols; aromatic hydrocarbons, like ethylbenzene, can be efficiently oxidized in the tandem catalytic system (PS-ISB/$RuCl_3$) but do not react in the PS-ISB/$BF_3\cdot OEt_2$ system (Table 1, entry 17).

Finally, we have investigated the use of iodinated polystyrene [PS-IB (**4**)] as a precatalyst to PS-ISB (**2**) in the tandem system PS-ISB/$RuCl_3$. As expected, PS-IB shows much lower catalytic activity compared to PS-ISB, since a slow initial oxidation of the ArI to the actual ArIO catalyst is required in this case.[12] In the presence of PS-IB/$RuCl_3$, carboxylic acids from primary alcohols and ketones from the secondary alcohols were obtained in low yields, while ethylbenzene and propylbenzene did not react at all.

In conclusion, we have prepared a novel polymer-supported iodosylbenzene (**2**), which can find practical application as a readily available, stable, and recyclable oxidant and catalyst. Treating alcohols with PS-ISB in the presence of $BF_3\cdot OEt_2$ allowed in most cases complete conversion into aldehydes or ketones, while treating anthracene led to anthraquinone in good yield, under mild conditions and with convenient workup. A tandem catalytic system (PS-ISB/$RuCl_3$) has been developed for the catalytic oxidation of alcohols and alkylbenzenes to corresponding carboxylic acids and ketones using Oxone as stoichiometric oxidant.

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## References and Notes

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(8) **Preparation of PS-ISB (2)**
PS-DIB (**1**,[7] 1.430 g, 3.0 mmol) and NaOH (0.400 g, 10.0 mmol) were grinded intensively in a mortar at r.t. for 10 min. The resulting mixture was left to stay at r.t. for 2 h, then $H_2O$ (15 mL) was added and stirred overnight, the mixture was filtered, washed with $H_2O$ (3 × 3 mL), acetone (3 × 3 mL), and $Et_2O$ (3 × 3 mL) subsequently, and then dried in vacuum to give a yellow powder (1.05 g). Elem. Anal. (%): O, 8.68; I, 37.19. IR (KBr): $\nu = 761$ (I=O) $cm^{-1}$.

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(10) **General Procedure for Oxidations Using PS-ISB (2)**
To a vigorously stirred suspension of PS-ISB (**2**, 0.3 mmol) in $CH_2Cl_2$ (2 mL), $BF_3\cdot OEt_2$ (0.040 mL) was added, and the resulting mixture was stirred at r.t. for 15 min. To the mixture, the appropriate alcohol (0.2 mmol) or $Ph_3P$ (0.2 mmol) or anthracene (0.1 mmol) was added. The resulting mixture was stirred at r.t. for the indicated time (Table 1). A portion of the crude reaction mixture (100 μL) was poured into a flask with $Et_2O$ (0.5 mL) to precipitate PS-IB, then the mixture was passed through a 2–3 cm of silica gel suspended in a Pasteur pipette, and the resulting solution was analyzed by GC-MS to determine the conversion of organic substrates.

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(13) **Typical Procedure of the PS-ISB/$RuCl_3$-Cocatalyzed Oxidation of Alcohols**
Oxone (0.92 g, 1.5 mmol) was added to a mixture of 1-phenylethanol (122 mg, 1 mmol, Table 2, entry **7**), PS-ISB (**2**, 0.070 g, 0.1 mmol, 10 mol%), and $RuCl_3$ (10 μL of 0.20 M solution in $H_2O$, 0.002 mmol, 0.2 mol%) in MeCN (3 mL) and $H_2O$ (3 mL) in one portions under stirring at r.t. (the reaction was monitored by TLC by the disappearance of 1-phenylethanol). Then EtOAc (15 mL) and $H_2O$ (20 mL) were added, and the mixture was stirred for 5 min. The polymeric catalyst (PS-ISB) was filtered, washed with $H_2O$ (2 × 2 mL) and EtOAc (2 × 2 mL), and collected for next run. The organic solution was separated, and the aqueous phase and extracted with EtOAc (2 × 15 mL). The organic solutions were combined, washed with NaCl (sat. solution, 20 mL), and dried over anhyd $Na_2SO_4$. Removal of the solvent under vacuum afforded acetophenone (114 mg, 95%). The oxidation of other alcohols and hydrocarbons (Table 2) was performed by using a similar procedure.