Introduction

The importance of hypervalent iodine reagents in organic chemistry has been demonstrated in recent years, and they have been found to have several desirable properties: they are mild, selective, efficient and eco-friendly.\(^1\) 2-Iodoxybenzoic acid (IBX) has been developed as a powerful reagent for several organic transformations, and a recent surge in interest was driven by the publication of an improved method for its synthesis.\(^2\) IBX is a powerful single-electron transfer oxidant that readily accepts a new heteroatom-based ligand, and has been applied successfully for the construction of novel heterocycles.

Preparation

According to a new improved procedure, IBX can be prepared in very good yield by the oxidation of 2-iodobenzoic acid with Oxone;\(^2\) this shows advantages over the previously reported methods.\(^2\)

Abstracts

(A) IBX oxidizes 1° and 2° alcohols to the corresponding aldehydes and ketones, without any over-oxidation, in DMSO at room temperature.\(^3\) Using different solvent systems and higher temperatures, yields of 90–100% can be obtained.\(^4\) Environmentally benign ionic liquids have also been used as solvents for this transformation.\(^5\)

(B) IBX has been used to oxidize oximes and tosyl hydrazones to the corresponding carbonyl compounds.\(^6\)
(C) IBX was used to oxidize saturated alcohols and carbonyl compounds\(^7\) to the corresponding \(\alpha,\beta\)-unsaturated carbonyl system in one pot. It can also be used to oxidize the benzylic position.\(^9\)

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{(IBX, 3.5 equiv)}} \text{O} \quad \text{IBX, 3.5 equiv} \\
65^\circ \text{C}, 4-24 \text{ h} & \quad \text{60-85\%} \\
& \quad \text{29 examples}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{(IBX, 1.5 equiv)}} \text{O} \quad \text{IBX, 1.5 equiv} \\
65^\circ \text{C}, 4-24 \text{ h} & \quad \text{40-80\%} \\
& \quad \text{29 examples}
\end{align*}
\]

(D) IBX reacts with certain unsaturated N-aryl amides (anilides) to form novel heterocycles such as \(\delta\)-lactams, cyclic urethanes, hydroxylamine and aminosugar building blocks.\(^8\)

\[
\begin{align*}
\text{Ar} & \xrightarrow{\text{IBX, THF-DMSO}} \text{X} \quad \text{X = O, CH\text{\_}2, NR} \\
(10^\circ), 90^\circ \text{C}, 24 \text{ h} & \quad 70-95\% \\
& \quad \text{29 examples}
\end{align*}
\]

(E) In combination with an N-oxide (MPO), IBX was used to oxidize a carbonyl\(^9\) and its silyl enol ether\(^9\) to the corresponding \(\alpha,\beta\)-unsaturated compounds in high yield at ambient temperature.

\[
\begin{align*}
\text{O} & \xrightarrow{\text{IBX-MPO (2-4 equiv)}} \text{O} \quad \text{IBX-MPO (2-4 equiv)} \\
\text{DMSO, r.t., 15-48 h} & \quad \text{70-96\%} \\
& \quad \text{17 examples}
\end{align*}
\]

(F) A regioselective oxidation of phenols to \(\alpha\)-quinones was performed with IBX.\(^10\)

(G) Recently, IBX was used to convert nitrogen- and sulfur-containing substrates to synthetically useful intermediates.\(^11\)

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{IBX, 1 equiv)}} \text{O} \\
r.t. & \quad 85-92\% \\
& \quad \text{11 examples}
\end{align*}
\]

\[
\begin{align*}
\text{H} & \xrightarrow{\text{IBX, 1.1 equiv)}} \text{O} \\
\text{DMSO, 45^\circ C} & \quad \text{80-98\%} \\
& \quad \text{17 examples}
\end{align*}
\]

\[
\begin{align*}
\text{R} & \xrightarrow{\text{IBX, 2 equiv)}} \text{O} \\
\text{H}_2\text{O-DMSO (1:9), 25^\circ C} & \quad \text{96-99\%} \\
& \quad \text{96-99\%}
\end{align*}
\]

References