

SYNLETT Spotlight 56

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Iodosobenzene (PhIO)

Compiled by Ana Minatti

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Introduction

The title compound is one of the most important oxygen transfer reagents for selective stoichiometric or catalytic oxy-functionalization.¹ The involvement of PhIO in numerous reactions such as the asymmetric alkene epoxidation,^{2,3} the asymmetric oxidation of sulfides^{3,4} and enol ether derivatives,^{3a,5} allylic⁶ and asymmetric benzylic C–H oxidation,^{3a,7} the chemoselective oxidation of alcohols and aldehydes to carbonyl compounds,⁸ the oxidation of amines⁹ and hydroquinones,¹⁰ among others, convincingly proves the versatility of this oxidizing agent.

PhIO is not only employed as a terminal oxidant, it may also serve as a mediator in aziridinations and cyclopropanations of alkenes,^{3a,11} in amidoglycosylations¹² and α -functionalizations of carbonyl compounds.¹³

PhIO is insoluble in most organic solvents due to its polymeric structure, therefore reactions with PhIO are usually carried out in water or methanol. The active monomeric species is also generated in the presence of Lewis acids like $\text{BF}_3 \cdot \text{Et}_2\text{O}$ or various transition metals, such as Fe(IV),^{2c,7a,4b} Mn(III),^{2b,3,14} Cr(III),^{2a,3,6} Rh(II)/(III),^{12,14b} Ru(II)/(III),^{8a,15} Cu(I)/(II),^{11,12} Yb(III),^{8b} Co(II),¹⁶ Ni(II),¹⁷ which serve as

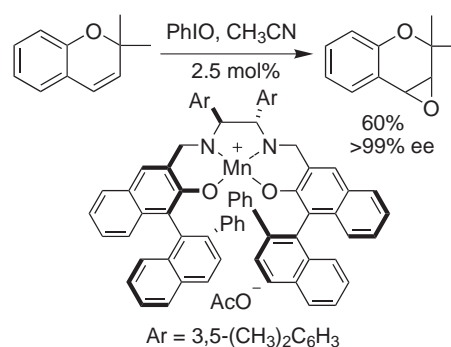
excellent catalysts for a wide range of oxidative transformations. Nevertheless, non-catalytic oxidations in aprotic solvents^{9a,18} and solid-state reactions of polymeric PhIO¹⁹ have also been reported. In most cases the oxidative properties of PhIO are related to the electrophilic reactivity of the hypervalent iodine centre. In transition metal complex-catalyzed oxygenations with PhIO an intermediate high-valent oxo complex is responsible for the final oxygen transfer. Additionally, PhIO serves as a precursor to various other iodine(III) compounds like iodosyl dihalides, dicarboxylates and disubstituted derivatives of strong acids.²⁰ Imidoiodanes, the formal analogs of iodosobenzene and azido-iodanes can also be conveniently synthesized from PhIO.²¹

Preparation of PhIO: Commercially available iodosobenzene diacetate is treated with aqueous sodium hydroxide to give pure PhIO as a yellowish amorphous powder after filtration and air-drying.²²

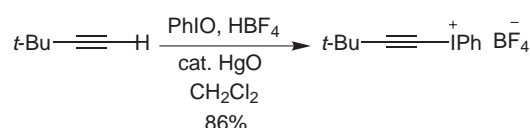
Precautions: PhIO explodes if heated to 210 °C due to disproportion into PhI and colorless, explosive iodylbenzene PhIO_2 .

Abstracts

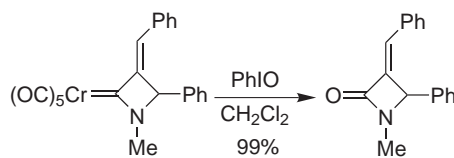
(A) The catalytic asymmetric epoxidation of olefins with chiral (salen)manganese(III) complexes represents the most popular reaction employing PhIO as a reactant. In particular, the oxidation of conjugated *cis*-olefins was achieved with remarkably high enantioselectivity using second generation Mn-salen complexes, bearing chiral binaphthyl subunits.²³



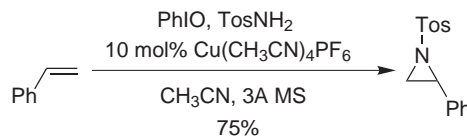
(B) A new and efficient method has been developed for the synthesis of alkenyl(aryl)iodonium salts. These versatile reagents could be isolated as stable BF_4 salts after treating the corresponding alkynes with iodosobenzene in the presence of HBF_4 and catalytic amounts of HgO .²⁴



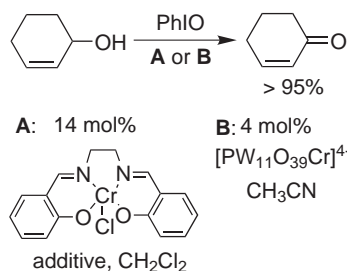
(C) The chemoselective oxidation of a Fischer carbene complex of pentacarbonylchromium(0) with PhIO was the decisive transformation in an alternative approach to β -lactams.²⁵



(D) Dauban et al. reported on copper-catalyzed aziridination of olefins in the presence of PhIO and *p*-toluenesulfonamide. This represents the first example of a catalytic nitrene-transfer onto prochiral olefins by in situ formation of the imidoiodane PhI=NTos.¹¹ Recently an intramolecular version of this reaction was applied to unsaturated sulfamates derived from primary and secondary alcohols.²⁶



(E) The catalytic chemoselective C–H oxidation of 2-cyclohexenol to 2-cyclohexenone in organic solvents without any epoxide formation was achieved either by the usage of a (salen)chromium(III) complex or a chromium-substituted α -Keggin-type polyoxo-metalate and PhIO as the terminal oxidant.^{6b} An environmentally benign oxidation of this substrate was realized by activating PhIO with only a small amount of water.^{8c}



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