

SYNLETT Spotlight 278

Iodoxybenzene (PhIO₂)

Compiled by Cai Zhang



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

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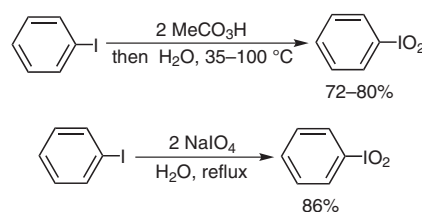
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Introduction

Iodoxybenzene (PhIO₂, mp 230 °C) is the first organic compound of iodine(V) prepared by Willgerodt 100 years ago.¹ Specifically, it can be prepared by disproportionation of iodosylbenzene under steam distillation.² Ten years ago iodoxybenzene has been used for the synthesis of cadalenquinone,^{3a} unsaturated carbonyl compounds^{3b-c}, oxodienes,^{3d-e}, epoxides,^{3f} quinine imines,^{3g} and sulfones.^{3h} In this Spotlight recent applications using PhIO₂ in organic syntheses are summarized.

Preparation

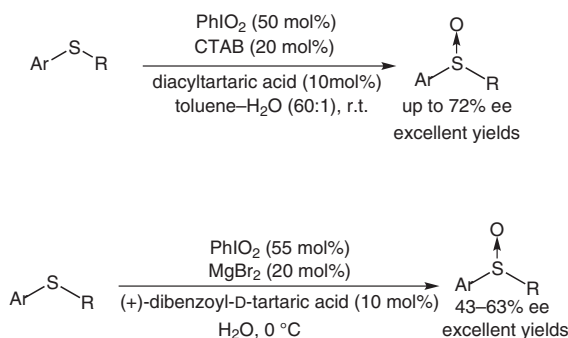
Iodoxybenzene (PhIO₂) can be directly prepared using commercial 40% peracetic acid or sodium periodate by dissolving iodobenzene in water (Scheme 1).⁴



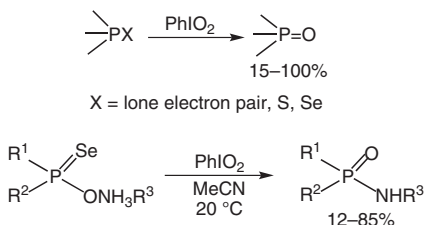
Scheme 1

Abstracts

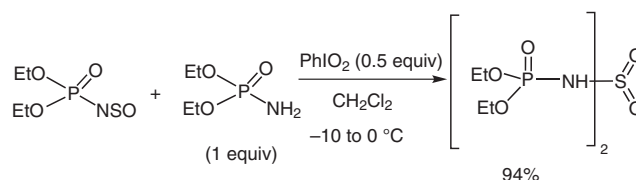
(A) Kita et al. show the solubilization and activation of PhIO₂ by adding catalytic amounts of both cetyltrimethylammonium bromide (CTAB) or MgBr₂ and a chiral tartaric acid derivative. Both reagents were indispensable for the enhancement of chemical and optical yields in the oxidation of sulfides to sulfoxides.⁵



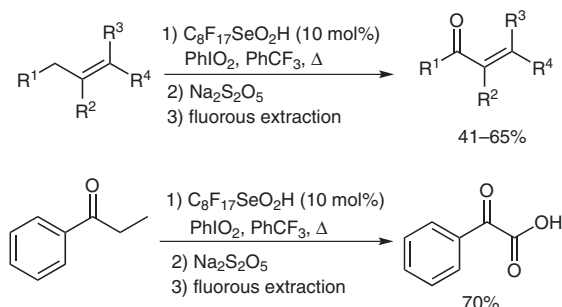
(B) The application of PhIO₂ in the oxidation reaction of phosphorous, phosphorothiono and phosphoroseleno compounds into the corresponding $\equiv\text{P}(\text{O})$ analogues was demonstrated by Lopusinski et al.^{6a} The direct conversion of ammonium dialkyl phosphoroselenoates into the dialkyl phosphoramidates using iodoxybenzene has been developed by the same group.^{6b}



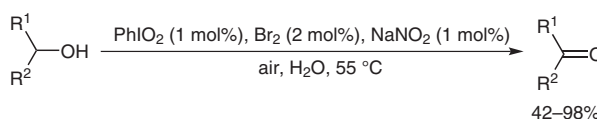
(C) The reaction performed between *N*-sulfinylphosphoramidate and PhIO_2 in the presence of diethylphosphoramidate results in the formation of *N,N*-bis(diethylphosphor)sulfamide.⁷



(D) Catalytic allylic oxidation of alkenes into enones and oxidation of aryl alkyl ketones into the corresponding ketoacids with a fluorous seleninic acid as catalyst in conjunction with PhIO_2 as reoxidant have been developed by Zou and co-worker.⁸



(E) Recently, air-driven conversion of alcohols into carbonyl compounds in water using catalytic amounts of PhIO_2 has been reported by Liu and co-workers.⁹



References

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