

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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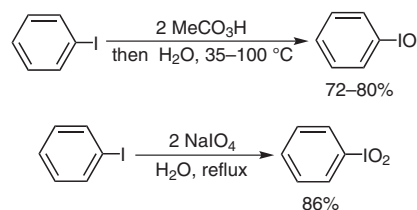
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Introduction

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}, oxidienes,^{3d-e}, epoxides,^{3f} quinine imines,^{3g} and sulfones.^{3h} In this Spotlight recent applications using PhIO₂ in organic syntheses are summarized.

Preparation

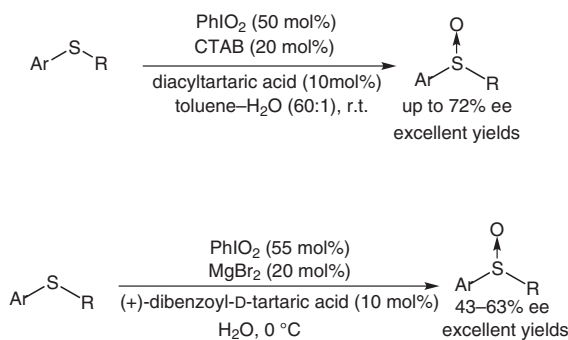
Iodoxybenzene (PhIO₂) can be directly prepared using commercial 40% peracetic acid or sodium periodate by dissolving iodobenzene in water (Scheme 1).⁴



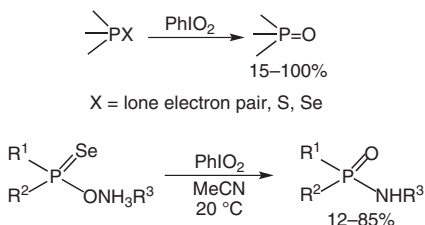
Scheme 1

Abstracts

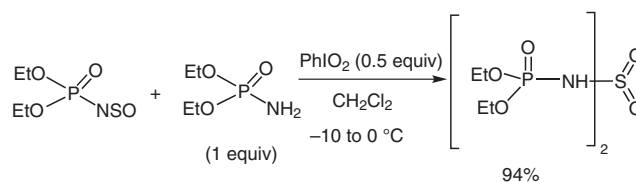
(A) Kita et al. show the solubilization and activation of PhIO₂ by adding catalytic amounts of both cetyltrimethylammonium bromide (CTAB) or MgBr₂ and a chiral tartaric acid derivative. Both reagents were indispensable for the enhancement of chemical and optical yields in the oxidation of sulfides to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



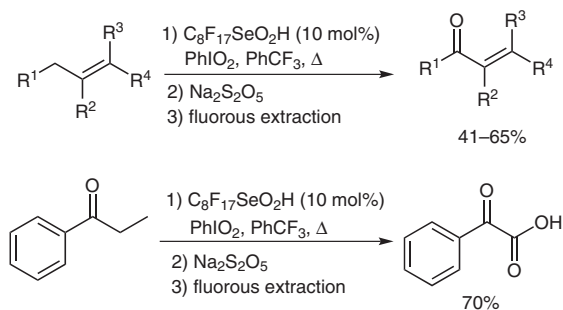
(B) The application of PhIO₂ in the oxidation reaction of phosphorous, phosphorothiono and phosphoroseleno compounds into the corresponding ≡P(O) analogues was demonstrated by Lopusinski et al.^{6a} The direct conversion of ammonium dialkyl phosphoro-selenoates into the dialkyl phosphoramidates using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



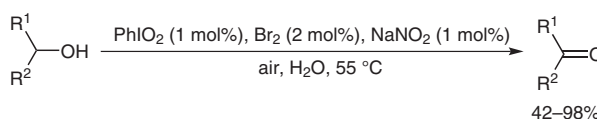
(C) The reaction performed between *N*-sulfinylphosphoramidate and PhIO_2 in the presence of diethylphosphoramidate results in the formation of *N,N*-bis(diethylphosphor)sulfamide.⁷



(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

- (1) Willgerodt, C. *Die Organischen Verbindungen mit Mehrwertigem Jod*; Enke Verlag: Stuttgart, **1914**.
- (2) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 154.
- (3) (a) Reddy, N.; Kesavulu, R. a. o.; G, S. K. *Indian J. Chem., Section B: Org. Chem. Incl. Med. Chem.* **1987**, *26B*, 920. (b) Barton, D. H. R.; Crich, D. *Tetrahedron* **1985**, *41*, 4359. (c) Gleiter, R.; Mueller, G. *J. Org. Chem.* **1988**, *53*, 3912. (d) Künzer, H.; Sauer, G.; Wiechert, R. *Tetrahedron* **1989**, *45*, 6409. (e) Iida, T.; Nishida, S.; Chang, F. C.; Niwa, T.; Goto, J.; Nambara, T. *Chem. Pharm. Bull.* **1993**, *41*, 763. (f) Barret, R.; Sabot, J. P.; Pautet, F.; Cerf, P.; Daudon, M. *Oxidation Communications* **1989**, *12*, 55. (g) Barret, R.; Daudon, M. **1990**, *20*, 1543. (h) Barret, R.; Pautet, F.; Bordat, P.; Tinland, B.; Daudon, M. *Phosphorus, Sulfur and Silicon and the Related Elements* **1989**, *45*, 31.
- (4) (a) Sharefkin, J. G.; Saltzman, H. *Org. Synth.* **1963**, *43*, 65. (b) Kazmierczak, P.; Skulski, L.; Kraszkiewicz, L. *Molecules* **2001**, *6*, 881.
- (5) (a) Tohma, H.; Takizawa, S.; Watanabe, H.; Fukuoka, Y.; Maegawa, T.; Kita, Y. *J. Org. Chem.* **1999**, *64*, 3519. (b) Tohma, H.; Takizawa, S.; Morioka, H.; Maegawa, T.; Kita, Y. *Chem. Pharm. Bull.* **2000**, *48*, 445.
- (6) (a) Mielniczak, G.; Lopusinski, A. *Synlett* **2001**, 505. (b) Mielniczak, G.; Lopusinski, A. *Heteroatom Chem.* **2003**, *14*, 121.
- (7) Mielniczak, G.; Lopusinski, A. *Heteroatom Chem.* **2008**, *19*, 530.
- (8) (a) Crich, D.; Zou, Y. *Org. Lett.* **2004**, *6*, 775. (b) Crich, D.; Zou, Y. *J. Org. Chem.* **2005**, *70*, 3309.
- (9) Mu, R. Z.; Liu, Z. Q.; Yang, Z. J.; Liu, Z. G.; Wu, L. M.; Liu, Z. L. *Adv. Synth. Catal.* **2005**, *347*, 1333.