

SYNLETT Spotlight 367

Polymer-Supported Hypervalent Iodine as Green Oxidant in Organic Synthesis



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

Compiled by Mosadegh Keshavarz

Mosadegh Keshavarz was born in 1980 in Dehdasht, Iran. He received a B.Sc. degree from the Teacher Training University of Tehran and after studying for three years at the Shahid Chamran University of Ahvaz, he obtained a M.Sc. degree in organic chemistry under the supervision of Professor Rashid Badri. He is continuing his Ph.D. under the supervision of Professor Rashid Badri and Fariba Haidari and is currently a visiting student at the University of Perugia. His research interest is focused on click reactions and polymer-supported catalysts in organic synthesis.

Chemistry Department, Shahid Chamran University, Ahvaz 61357-4-3169, Iran

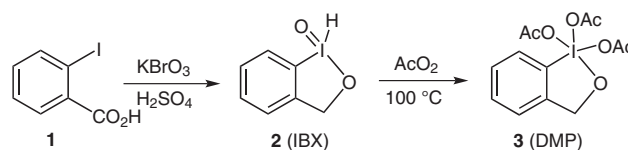
E-mail: m-keshavarz@scu.ac.ir

Dedicated to Professor Hossein Aghabozorg.

Introduction

2-Iodoxy benzoic acid (IBX) and Dess–Martin periodinane (DMP, Scheme 1) have been extensively employed in organic synthesis as mild and highly selective reagents for the oxidation of alcohols to carbonyl compounds as well as for a variety of other synthetically useful oxidative transformations. However, IBX and DMP are not perfect with respect to the principles of green chemistry since they are normally used as non-recyclable, stoichiometric reagents in non-recyclable organic solvents, which have potentially damaging environmental effects.^{1,2} Reactions of monomeric hypervalent iodine reagents with organic substrates lead to the respective iodoarenes as byproducts, which in general are not recoverable from a reaction mixture. The discovery of recyclable reagents and catalytic systems based on the iodine redox chemistry has initiated

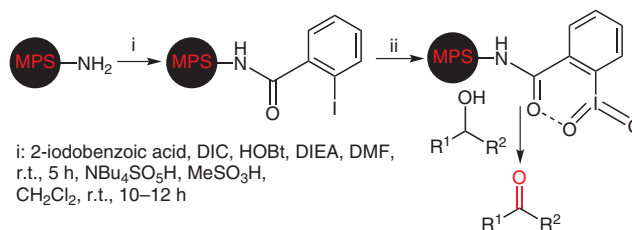
a major surge of research activity and added a new dimension to the field of hypervalent iodine chemistry. Polymer-supported modifications of hypervalent iodine reagents retain the useful reactivity of their monomeric analogues with the added advantage of being readily recyclable and reusable. Numerous new organoiodine(V) reagents have recently been developed, and it is anticipated that these safe and efficient derivatives and analogues of IBX will find widespread synthetic application in the future.



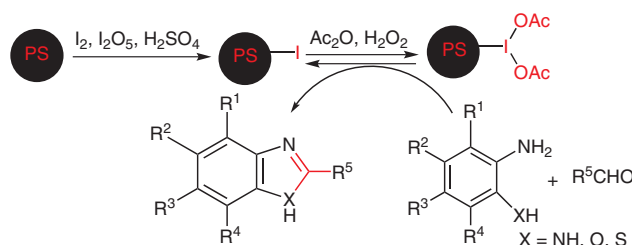
Scheme 1 Preparation of IBX and DMP

Abstracts

(A) Jang et al. used macroporous polystyrene-supported IBX (MPS–IBX) amides to convert a range of alcohols into corresponding carbonyl compounds in various solvents. Polymer supported IBX was prepared in two simple steps, and the polymeric reagent was then evaluated for its efficiency. The results indicated that the MPS–IBX amides were compatible with a variety of solvents.³



(B) Kumar et al. reported polystyrene-supported hypervalent iodine as new recyclable and reusable heterogeneous catalyst for diversity-oriented synthesis of benzimidazole and benzoxa/(thia)zole libraries.⁴



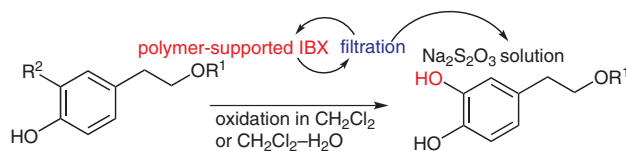
SYNLETT 2011, No. 16, pp 2433–2434

Advanced online publication: 14.09.2011

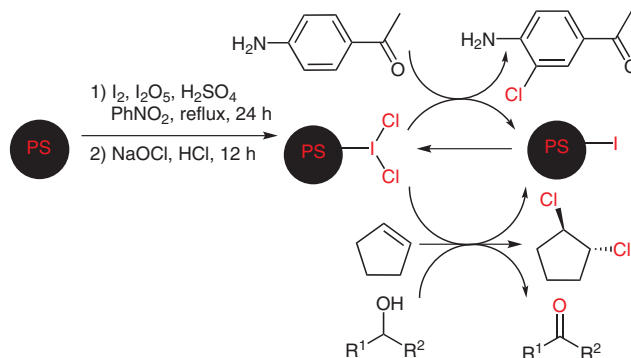
DOI: 10.1055/s-0030-1261234; Art ID: V37411ST

© Georg Thieme Verlag Stuttgart · New York

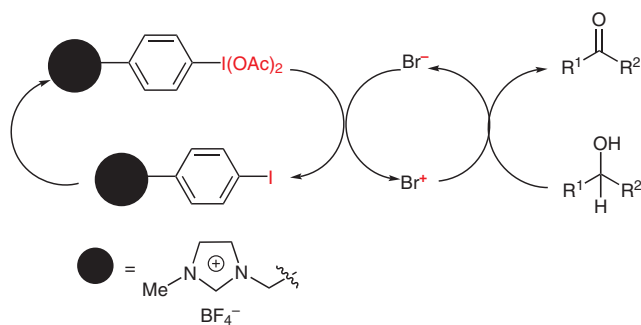
(C) A useful and novel application of polymer-supported IBX for the chemoselective and regioselective oxidation of phenolic compounds has been described. Hydroxytyrosol and carboxymethylated hydroxytyrosol have been prepared in good conversions and yields under green-chemistry conditions in the presence of dimethyl carbonate as solvent. The polymer-supported reagent has been recovered by simple filtration, regenerated, and reused for more cycles of oxidation reactions without loss of efficiency.⁵



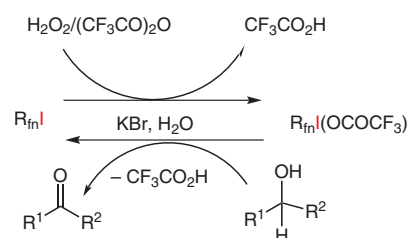
(D) Polystyrene-supported (dichloroiodo)benzene (loading of ICl_2 up to 1.35 mmol/g) from polystyrene, iodine and bleach has been developed. This recyclable reagent is useful for efficient chlorination of organic substrates and selective oxidation of various alcohols to the carbonyl compounds in high yields under mild conditions.⁶



(E) The ion-supported hypervalent iodine reagent has been used as a recoverable and reusable oxidant for the oxidation of primary alcohols to carbonyl compounds. The aldehydes do not undergo further oxidation to carboxylic acids even at longer reaction times. The reagent can be recovered and reused after oxidation with peracetic acid.⁷



(F) Reactions of commercial fluorous alkyl iodides $\text{R}_{\text{fn}}\text{I}$ ($1-\text{R}_{\text{fn}}$; $\text{R}_{\text{fn}} = \text{CF}_3(\text{CF}_2)_{n-1}$; $n = 7, 8, 10, 12$) with 80% H_2O_2 and trifluoroacetic anhydride give $\text{R}_{\text{fn}}\text{I}(\text{OCOCF}_3)_2$ ($2-\text{R}_{\text{fn}}$; 89–97% yield). These efficiently oxidize aliphatic and benzylic secondary alcohols into the corresponding ketones (57–92% yield) in the presence of aqueous KBr and in the absence of organic or fluorous solvents. After the final cycle, 57–59% of the original charge of the fluorous iodide species has been recovered.⁸



References

- (1) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press Inc.: New York, **1998**.
- (2) (a) Mülbaier, M.; Giannis, A. *Angew. Chem. Int. Ed.* **2001**, *40*, 4393. (b) Sorg, G.; Mengei, A.; Jung, G.; Rademann, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4395. (c) Lei, Z. Q.; Ma, H. C.; Zhang, Z.; Yang, Y. X. *React. Funct. Polym.* **2006**, *66*, 840. (d) Lei, Z.; Denecker, C.; Jegasothy, S.; Sherrington, D. C.; Slater, N. K. H.; Sutherland, A. J. *Tetrahedron Lett.* **2003**, *44*, 1635. (e) Bromberg, L.; Zhang, H.; Hatton, T. A. *Chem. Mater.* **2008**, *20*, 2001.
- (3) Jang, H. S.; Chung, W. J.; Lee, Y. S. *Tetrahedron Lett.* **2007**, *48*, 3731.
- (4) Kumar, A.; Maurya, R. A.; Ahmad, P. *J. Comb. Chem.* **2009**, *11*, 198.
- (5) Bernini, R.; Mincione, E.; Barontini, M.; Crisante, F.; Fabrizi, G. *Tetrahedron Lett.* **2009**, *50*, 1307.
- (6) Chen, J. M.; Zeng, X. M.; Middleton, K.; Zhdankin, V. V. *Tetrahedron Lett.* **2011**, *50*, 1952.
- (7) Qian, W.; Jin, E.; Bao, W.; Zhang, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 952.
- (8) Tesevic, V.; Gladysz, J. A. *J. Org. Chem.* **2006**, *71*, 7433.