

SYNLETT Spotlight 217

[Hydroxy(tosyloxy)iodo]benzene (HTIB)

Compiled by Rajesh Kumar



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

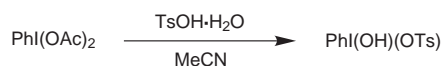
Rajesh Kumar was born in 1980 at Karsa Dod, Haryana, India. He received his B.Sc. and M.Sc. degrees in chemistry with specialization in organic chemistry from Kurukshetra University, Kurukshetra, Haryana, India. Presently he is working as a Senior Research Fellow (CSIR-SRF) towards his PhD under the supervision of Prof. Om Prakash at Kurukshetra University. His research work is focused on the synthetic utility of hypervalent iodine(III) reagents in organic synthesis.

Department of Chemistry, Kurukshetra University, Kurukshetra, Haryana 136119, India
E-mail: rajesh_chem12a@rediffmail.com

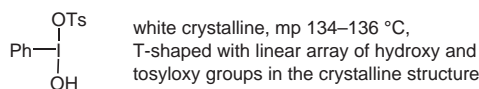
Introduction

[Hydroxy(tosyloxy)iodo]benzene (HTIB), one of the most significant reagents among the family of hypervalent iodine reagents, has been widely used as an effective oxidant in the synthesis of various organic compounds. HTIB was first discovered in 1970 by Neiland and Karele.¹ A few years later, Koser and co-workers discovered that HTIB is an efficient reagent in organic synthesis, so in contemporary literature HTIB is often referred to as 'Koser's Reagent'.²

Preparation:

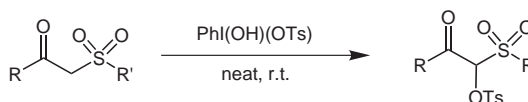


Properties:

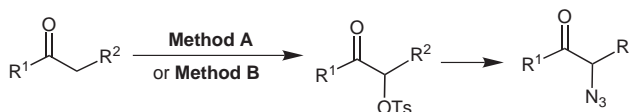


Abstracts

(A) A facile, general and high-yielding protocol for the synthesis of novel α -tosyloxy β -keto sulfones is described utilizing the relatively non-toxic HTIB under solvent-free conditions at room temperature.²



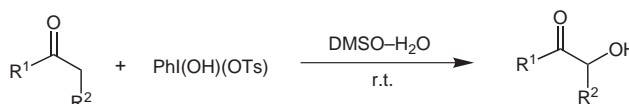
(B) Reaction of various ketones with HTIB followed by treatment of the α -tosyloxy ketones thus generated in situ with sodium azide, possibly in the presence of a phase-transfer catalyst, at room temperature offers a one-pot procedure for the synthesis of α -azido ketones.^{3,4}



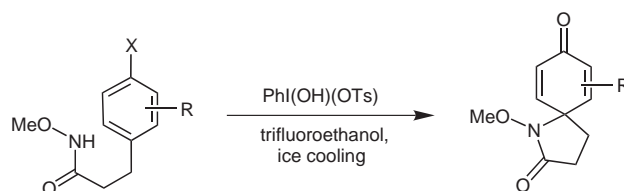
Method A: (i) HTIB, MeCN, reflux, 2 h; (ii) NaN₃, r.t., 2–3 h

Method B: HTIB, NaN₃, tetrabutylammonium bromide, r.t.

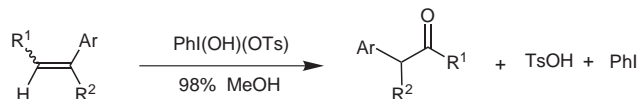
(C) Ketones react with HTIB in DMSO–H₂O to afford α -hydroxy ketones under neutral conditions and in good yields.⁵



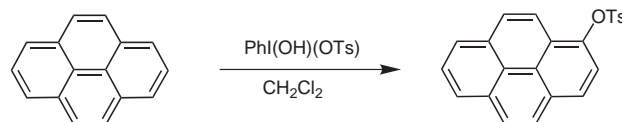
(D) Spirodienones bearing a 1-azaspiro[4.5]decane ring have been synthesized from *N*-methoxy-(4-halogenophenyl)amides by the intramolecular *ipso* attack of a nitrenium ion generated with HTIB in trifluoroethanol.⁶



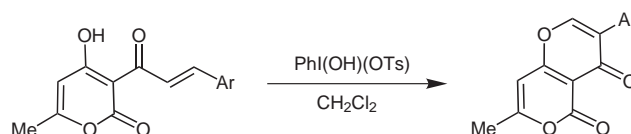
(E) The treatment of aryl alkenes with HTIB in 95% methanol affords the corresponding α -aryl ketones. This oxidative rearrangement is general for acyclic and cyclic aryl alkenes and permits regioselective synthesis of isomeric α -phenyl ketone pairs.⁷



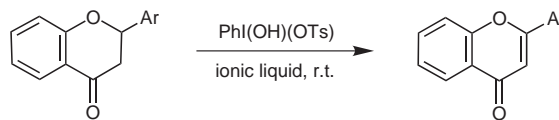
(F) Polycyclic aromatic hydrocarbons (PAH) undergo regioselective oxidative substitution with HTIB in dichloromethane to give the corresponding aryl sulfonate esters.⁸



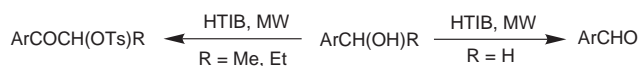
(G) Oxidation of 3-cinnamoyl-4-hydroxy-6-methyl-2*H*-pyran-2-ones with HTIB in CH₂Cl₂ leads to cyclization, thereby providing a new and convenient route for the synthesis of 3-aryl-7-methylpyrano[4,3-*b*]pyran-4*H*,5*H*-diones.⁹



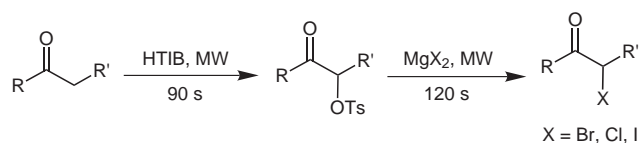
(H) Oxidation of flavanones to flavones was developed using HTIB in ionic liquid 1,3-di-*n*-butylimidazolium bromide at room temperature.¹⁰



(I) The oxidation of benzylic alcohols with HTIB provides a rapid and convenient method to prepare corresponding carbonyl compounds under solvent-free conditions.¹¹



(J) A novel and direct method for the synthesis of α -halocarbonyl compounds using sequential treatment of carbonyl compounds with HTIB followed by magnesium halides under solvent-free conditions.¹²



References

- (1) Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 889.
- (2) Kumar, D.; Sundaree, S.; Patel, G.; Rao, V. S.; Varma, R. S. *Tetrahedron Lett.* **2006**, *47*, 8239.
- (3) Prakash, O.; Pannu, K.; Prakash, R.; Batra, A. *Molecules* **2006**, *11*, 523.
- (4) Kumar, D.; Sundaree, S.; Rao, V. S. *Synth. Commun.* **2006**, *36*, 1893.
- (5) Xie, Y. Y.; Chen, Z. C. *Synth. Commun.* **2002**, *32*, 1875.
- (6) Miyazawa, E.; Sakamoto, T.; Kikugawa, Y. *J. Org. Chem.* **2003**, *68*, 5429.
- (7) Justik, M. W.; Koser, G. F. *Tetrahedron Lett.* **2004**, *45*, 6159.
- (8) Koser, G. F.; Telu, S.; Laali, K. K. *Tetrahedron Lett.* **2006**, *47*, 7011.
- (9) Prakash, O.; Kumar, A.; Sadana, A. K.; Singh, S. P. *Synthesis* **2006**, 21.
- (10) Muthukrishnan, M.; Patil, P. S.; More, S. V.; Joshi, R. A. *Mendeleev Commun.* **2005**, 100.
- (11) Lee, J. C.; Lee, J. Y.; Lee, S. J. *Tetrahedron Lett.* **2004**, *45*, 4939.
- (12) Lee, J. C.; Park, J. Y.; Yoon, S. Y.; Bae, Y. H.; Lee, S. J. *Tetrahedron Lett.* **2004**, *45*, 191.