SYNLETT
Spotlight 154

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

(Diacetoxy)iodobenzene

Compiled by Yue-dong Lu

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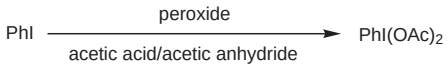
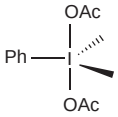
Introduction

(Diacetoxy)iodobenzene (DIB), one of the most significant species among the family of hypervalent iodines, has been widely used as an effective oxidant in synthesis of various compounds, especially those containing heteroatoms like N and O. According to the mechanism, the oxidation can be generally classified as either ionic-type or radical-type. In the latter, the oxidations are usually carried out in the presence of molecular iodine. Both can be utilized to prepare compounds through oxidative ring-opening or cyclic closure. DIB can also be applied to other types of reaction, such as electrophilic addition and bromination.

Preparation



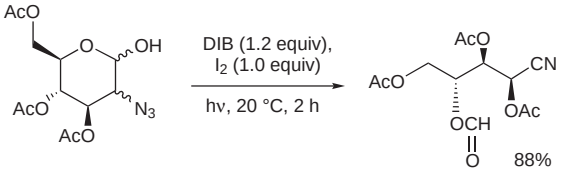
Properties



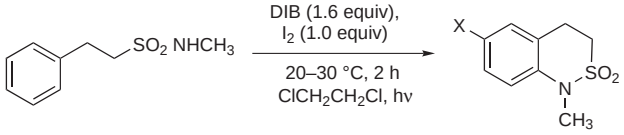
White microcrystalline powder, mp 160–161 °C, T-shape with a linear array of two acetoxy groups in the crystalline structure.

Abstracts

(A) Highly functionalized nitriles have been synthesized by an alkoxy radical fragmentation of cyclic β-hydroxy azides under mild conditions with DIB and iodine.[1]

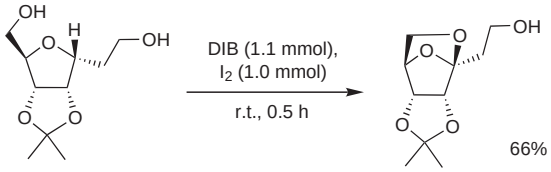


(B) A new preparative method for 3,4-dihydro-2,1-benzothiazine 2,2-dioxides from *N*-alkyl 2-(aryl)ethanesulfonamides with DIB and iodine under photochemical conditions has been described.[2]



X = H 0–95%
X = I 0–89%

(C) The reaction of specifically protected anhydroalditols with DIB and iodine is a mild and selective procedure for the synthesis of chiral 2,7-dioxabicyclo[2.2.1]heptane ring systems under neutral conditions.[3]



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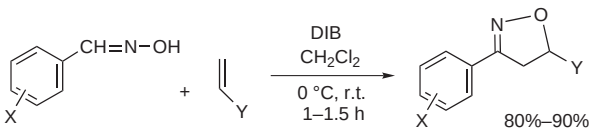
(D) Treatment of aldoximes with activated alkenes in the presence of DIB afforded isoxazolines smoothly in high yields and under very mild conditions.[4]

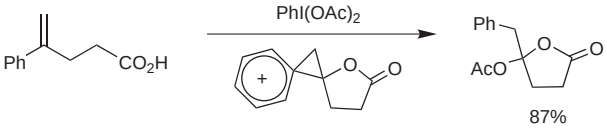


X = 3-NO_2, 3-OH, 2-Cl, Y = –$COOCH_3$, –CN, –$OCOCH_3$

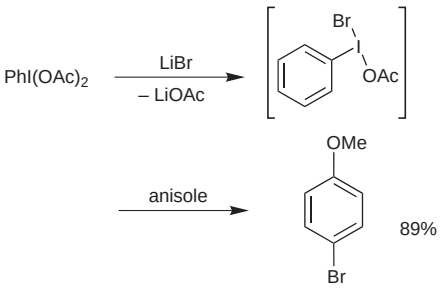
(E) Mamaeva et al. reported the first example that 1,2,4-thiadiazoles derivatives could be obtained in good to excellent yield by the oxidation of 1-monosubstituted thioureas with DIB.[5]

R = Ac	2PhI$(OAc)_2$/$CHCl_3$, 20 °C, 4 h	41%
R = Ph	2PhI$(OAc)_2$/MeCN, 20 °C, 30 min	55%

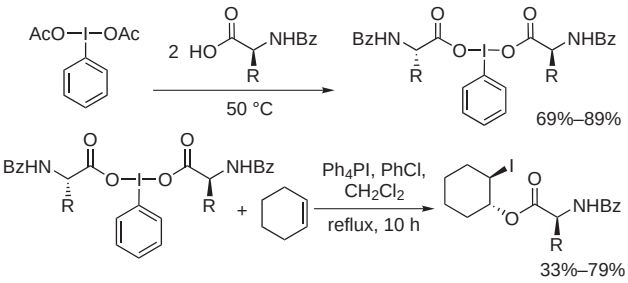
(F) A novel lactonization of 4-arylpent-4-enoic acids is described using DIB for the electrophilic addition onto a double bond. The hypervalent iodine species acts as a hypernucleofuge, generating intermediate phenonium ions, which react to form aryl-migrated lactones.[6]



(G) Mild bromination of olefins and activated arenes can be carried out in situ by the generation of 'Br$^+$' using DIB and LiBr.[7]



(H) Some new amino acid-derived iodobenzene dicarboxylates have been prepared by the reaction of DIB with N-protected natural amino acids through ligand exchange. These compounds in the presence of iodide anion can be used as reagents for β-iodocarboxylation of alkenes leading to the respective amino acid esters.[8]



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