SYNLETT
Spotlight 377

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

Molecular Iodine

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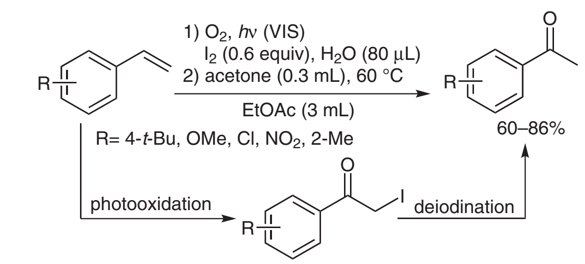
Introduction

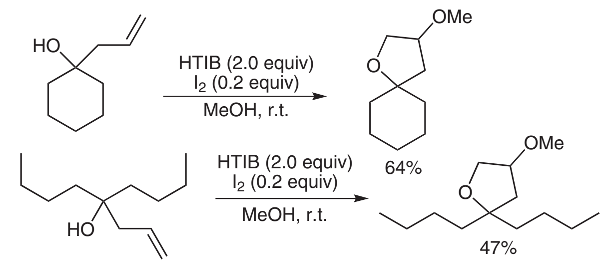
Molecular iodine is a bluish-black solid under standard conditions. It is highly soluble in nonpolar organic solvents and only slightly soluble in water owing to its lack of polarity. However, the solubility in water may be substantially increased in the presence of dissolved iodides due to the formation of triiodide ions. Since first discovered by Bernard Courtois in 1811[1b] the interest in utilization of molecular iodine in organic chemistry has increased dramatically due to its readily available, convenient, relatively cheap and environmental benign characteristics over the toxic heavy metals or complex regents. Many types of reactions can be promoted by iodine,[1,2] such as the oxidation of alcohols, C–C/C–N bond formation and formation of heterocycles, etc.

Abstracts

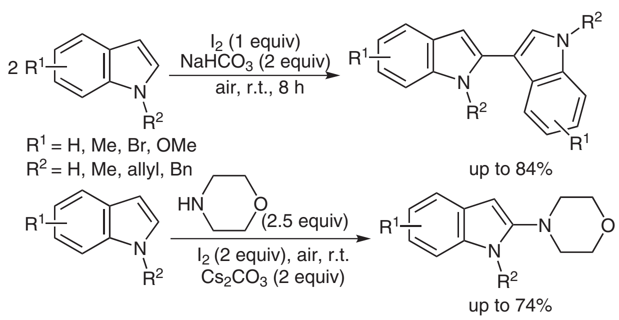
(A) Instead of the traditional palladium-catalyzed Wacker oxidation, Itoh and co-workers[3] have reported an one-pot synthetic protocol of acetophenones from styrenes with molecular iodine, visible light and oxygen. Regardless of various substituents at the aromatic ring, the corresponding acetophenones could be obtained in moderate to good yields. This procedure involves aerobic photooxidation and deiodination in one pot and provides the first report of metal-free direct syntheses of acetophenones from styrenes.



(B) By employing catalytic amount (10 mol%) of I_2 and [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent), Giannis et al.[4] have described a new and efficient synthetic method for diverse tetrahydrofuran derivatives. Compared to the previous systems such as Pd(II)/DIB[5] or $NaIO_4/NaHSO_3$,[6] the present methodology exhibits its obvious advantages; it is a one-step, metal-free and simple operation and has also great applicability in the synthesis of biologically active natural products.



(C) Iodine-induced regioselective C–C and C–N bond forming reactions of N-protected indole derivatives were reported by Liang and co-workers.[7] Compared with the transition-metal-catalyzed cross-couplings requiring noble metal catalysts and high loading of metal oxidants, the novel coupling method has shown great potential for both industrial and academic purposes.



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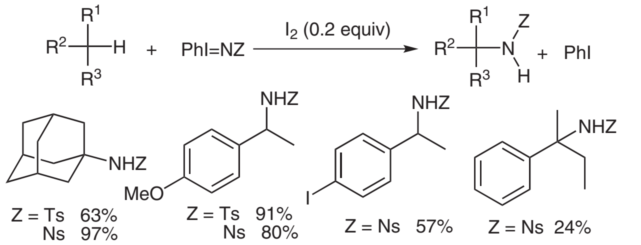
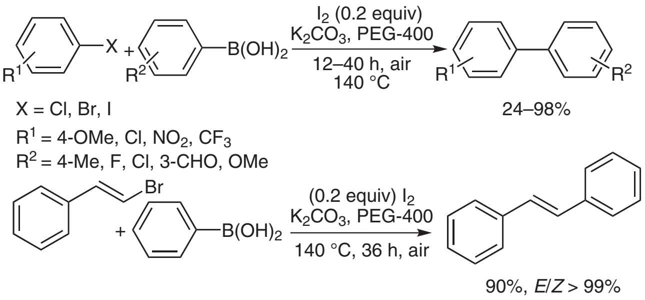
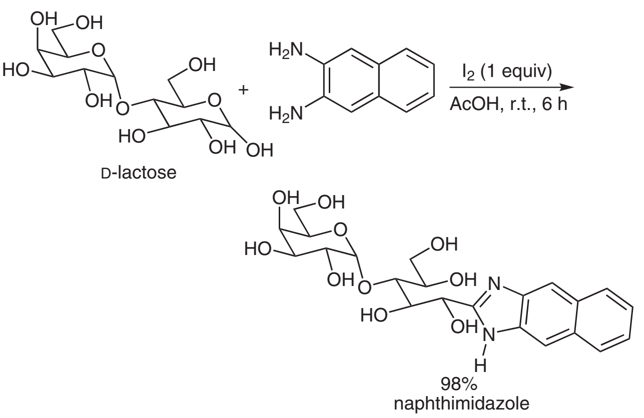
(D) Nicholas and co-workers[8] have disclosed an I_2-catalyzed aminosulfonating system for a broad range of benzylic and some types of saturated hydrocarbons utilizing imido-iodinanes ($PhI = NSO_2Ar$) as aminosulfonating reagent. It was worth to mention that the reaction was highly regioselective for the tertiary C–H of adamantine with no secondary C–H aminated product detected. While in some previous reported transition-metal-catalyzed systems,[9] the regioselectivity was relatively poor and the ratio of tertiary to secondary aminated products was 3–15:1.



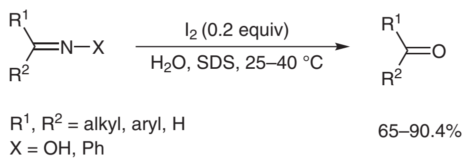
(E) Mao et al.[10] have found that the transition-metal-catalyzed Suzuki coupling could also be well performed in air using iodine as effective catalyst. In addition, the newly developed metal-free protocol was also applicable for the coupling of (*E*)-β-bromostyene with phenylboronic acid, with retention of the double bond geometry.



(F) Benzimidazole is an important chemical entity in pharmaceuticals due to its structural similarity to purine. In order to obtain this useful reagent, Lin et al.[11] have developed an efficient method for the conversion of unprotected and unmodified aldoses into aldobenzimidazoles and aldo-naphthimidazoles using iodine as oxidant. A series of mono-, di-, and trialdoses containing carboxyl and acetamido groups were introduced into the reaction given the desired products in high yields. Notably, no cleavage of the glycosidic bond occurred under such mild reaction conditions.



(G) Molecular iodine can also be used for deprotection. Konwar and co-workers[12] found that the I_2/SDS/water system could transform a broad range of oximes and imines to the corresponding carbonyl compounds with moderate to good yields under neutral conditions. it was found that the catalytic amount of I_2 could promote the reaction in the presence of surfactant (SDS), meanwhile, no formation of iodoxime/imidoyl iodide or over-oxidized products (acids) were observed during the reaction.



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