Iodine/TBHP

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Introduction

In recent times, several advancements were made in using catalytic amounts of iodine in combination with tert-butyl hydroperoxide (TBHP) as co-oxidant. The increased utility is mainly due to its inexpensive, environmentally benign nature, good efficiency and compatibility to work in place of rare or toxic heavy metal oxidants.1 The I2/TBHP catalytic system works efficiently for numerous C–C and C–X (X = heteroatom) bond-forming organic transformations under mild reaction conditions to offer the desired products in excellent yields.2

Table 1 Use of Iodine–TBHP

(A) Jiang et al. reported an I2/TBHP mediated domino oxidative cyclization for the one-pot synthesis of polysubstituted oxazoles from readily available styrenes and benzylamines under mild conditions.3

(B) Zhang et al. demonstrated the synthesis of 2-phenylquinazolines in good to excellent yields via tandem sp3 C–H functionalization of 2-amino benzophenones and benzylic amines.4

(C) Manjunath and Prabhu reported a metal-free catalytic route to 2-aminobenzoxazoles by amination of benzoxazoles via C–H bond activation of primary or secondary amines. Further the methodology was demonstrated to synthesize therapeutically active benzoxazoles.5

(D) An I2/TBHP catalyzed first efficient and direct synthesis of tertiary amides from alcohols and dimethylformamide has been developed. This transition-metal-free protocol provides a practical synthetic tool for the construction of N,N-dimethyl-substituted amides.6
(E) A metal-free oxidative coupling of methyl ketones and primary or secondary amines to α-keto amides was developed by Wan and his group. Four types of intermediates, α-iodo ketones, α-amino ketones, iminium intermediates and α-hydroxy amines were identified through a series of control experiments. The atom-economic methodology can be scaled-up, tolerates a variety of functional groups, and is operationally simple.7

(F) A novel I₂/TBHP catalyzed selective 2-arylsulfonylation of indoles was demonstrated. Various substituted 2-arylsulfonyl indoles were obtained in good to excellent yields in one pot. The direct sulfonylation reaction occurred selectively at C-2 position of the indole ring and only a catalytic amount of iodine acted as an efficient promoter. This method is a novel alternative approach for the synthesis of biologically important hetero diaryl sulfones from sodium sulfinitates.8

(G) Recently, we have developed an I₂/TBHP mediated synthesis of isatin and iodoisatin from 2′-aminoacetophenone via intramolecular oxidative amidation of the sp³ C–H bond. The reaction proceeds through sequential iodination, Kornblum oxidation, and amidation in one pot. The stoichiometric amount of I₂ plays a significant role in delivering iodoisatin exclusively in high yields.9

(H) Ji’s research group reported an I₂/TBHP mediated oxidation of commercially available indoles to isatins in moderate to good yields.10

References

1. (a) Finkbeiner, P.; Nachtsheim, B. J. Synthesis 2013, 979.