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Molecular iodine

Compiled by Mayuri M. Naik

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

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Introduction

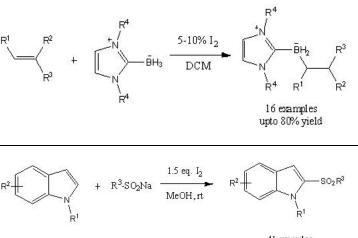
Iodine has gained considerable attention due to its ready availability, non-toxicity, cheap availability, easy handling and stability to air and moisture [1]. As a result it has become a preferred alternative for toxic and expensive metal catalysts in organic synthesis.

Abstracts

(A) Curran and co-workers have developed molecular iodine catalyzed reaction for the hydroboration of structurally diverse type alkenes by assorted Nheterocyclic carbene boranes. Replacement of sensitive and expensive triflimide [4] with easy to handle and inexpensive iodine, monohydroboration rather than dihydroboration and large substrate scope makes this method superior [5].

(B) A facile and highly efficient method for direct C2 sulfonylation reaction of indoles with sodium sulfinate mediated by iodine is described by Kuhakarn and coworkers. Mild reaction conditions, ease of operation and broad substrate scope are few advantages of this methodology [6].

It is a mild Lewis acid and a large number of heterocycles have been synthesized by iodine mediated domino [2] or one-pot multicomponent reactions [3]. Molecular iodine is used for various purposes such as oxidation, formation of carbon-carbon, carbon-nitrogen bonds, synthesis of heterocycles, etc. starting from catalytic amounts to higher stoichiometric levels.



41 examples upto 96% yield (C) Narender and co-workers have reported the formation of benzimidazoles and benzothiazoles using iodine. Also discovered the unprecedented formation of a new class of 2-benzyl-3-phenyl-3,4-dihydro-2*H*-benzo[e][1,2,4]thiadiazines mediated by iodine. The products were obtained in good to excellent yields [7].

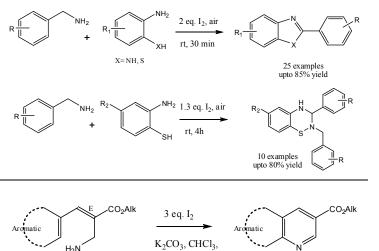
(**D**) An unexpected synthesis of aromatic ring annulated pyridines is reported by Batra and co-workers via an intramolecular electrophilic aromatic cyclization of suitably substituted primary allylamines mediated by molecular iodine under mild reaction conditions [8].

(E) Molecular iodine catalyzed oxidative C-C bond formation by a cross-dehydrogenative coupling reaction between tertiary amines and a carbon nucleophile in presence of aq. H_2O_2 as the terminal oxidant is explored by Itoh and co-workers. This is the first report on CDC reaction between two sp³ C-H bonds [9].

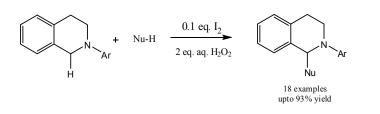
(F) Aryl methyl ketones, β -keto esters or styrenes in combination with α -amino acids can be efficiently converted to highly substituted oxazoles by molecular iodine catalyst via a decarboxylative domino reaction. Nachtsheim and co-workers reported this first synthesis of iodine catalyzed 2-alkyl-substituted oxazoles [10].

(G) Tian and co-workers demonstrated the sulfenylation reaction of indoles with sulfonyl hydrazides through the cleavage of sulphur-oxygen and sulphur-nitrogen bonds in presence of catalytic iodine. Diverse indole thioethers were achieved in high regioselectivity from several aryl, heteroaryl and alkylsulfonyl hydrazides in moderate to excellent yields [11].

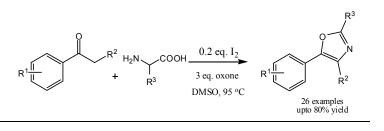
(H) Synthesis of 4-aryl-3,4-dihydrobenzopyran-2-ones [12] and 2-substituted or 2,2-disubstituted chromans [13] *via* [3+3] cyclocoupling using catalytic iodine is carried out by Tilve and co-workers. Our group prepared a series of compounds including naturally occurring dihydrolapachenole.

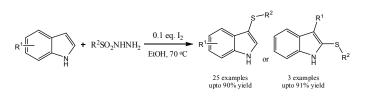


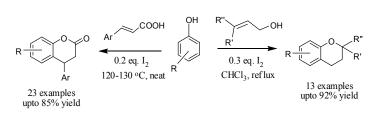
24 examples upto 84% yield



rt 30 min







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