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Use of heterogeneous catalysts in benzimidazole synthesis

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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.

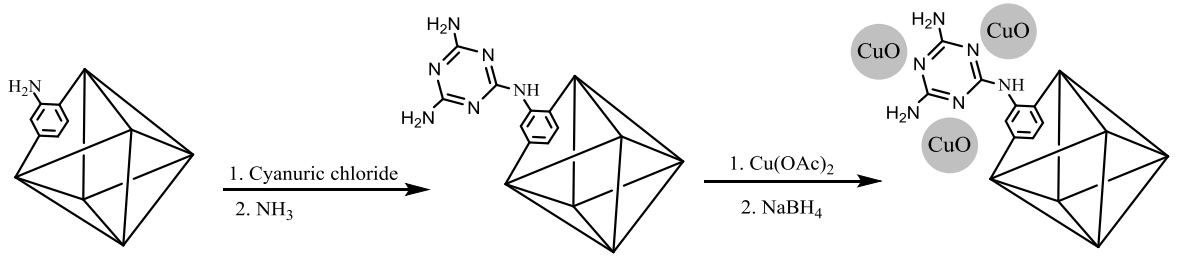
Introduction

In recent years, Benzoazoles and their derivatives have been of much significance due to their medical, physiological and biological properties [1] they are found in antiviral, antiulcer, antifungal, antihypertensive, anticancer, antihistamine anti-inflammatory, [2,3] antidepressant, antitumor, antifungal, antimycotic, antibiotic, antiulcerative, antibacterial and anti-allergic [4] compounds. Benzimidazoles and their derivatives are also known to be the key reaction intermediates in organic synthesis [5] for which two general methods have been reported. They include condensation of 2-aminothiophenol or 1,2-phenylenediamine with carboxylic acids or their derivatives (nitriles, imidates, or ortho-esters) [6] in the presence of strong catalysts like Bronsted and Lewis acids ($AlCl_3$ and BF_3) [7] and the oxidative cyclization of 1,2-phenylenediamine and 2-aminothiophenol with aldehydes [8]. The later method implies broad applicability due to the existence of a wide variety of aldehydes and oxidative reagents (i.e. nitrobenzene, 1,4-benzoquinone, air, hetero-poly acids, MnO_2, $Pb(OAc)_4$, H_2O_2/HCl etc.). [9]. Despite all the advantages of these methods, there also exist some drawbacks which include the requirement of strong acidic conditions, high reaction temperatures, prolonged reaction times, unsatisfactory yields, high cost, time-taking work-up, and the formation of the side products. Apart from the drawbacks, homogeneous catalysts modifications in the work-up procedure and inability to recover them have become a real challenge in the synthesis of benzimidazoles for the chemists. To solve these problems, several methods have been developed for the synthesis of benzoazoles, [10] among which dehydrogenative coupling of alcohols with phenols using heterogeneous catalysts (Ir (2.0wt%)/CeO_2, (PNNH) CoICl, Pt/TiO_2, Pt/Al_2O_3, $Ru_2Cl_4(CO)_6$) has proved as one of the most effective synthetic pathways [11]. In fact, the use of heterogeneous catalysts, i.e., different oxide based supported or unsupported catalysts including aluminosilicates [12], iron oxide [13], cobalt oxide [14], ZnO [15], CuO [16] and MoO_3 [17] have been recently of much interest in the synthesis of various benzimidazole derivatives due to their environmentally-friendly nature, room temperature, shorter reaction time, excellent yields (e.g. 2-aryl-1-arylmethyl-1H-

benzimidazoles by the use of highly reusable Amberlite IR-120 in aqueous media), good stability, and activity. Most heterogeneously catalyzed methods, however, require high catalyst loadings and development of expensive sophisticated catalysts. For example, expensive gold catalysts (e.g. TiO_2, Al_2O_3, ZnO, poly-urea and hydro-talcite) have been used for the synthesis of benzimidazoles from 2-nitroanilines under mild reaction conditions [18]. 2-nitroanilines was hydrogenated to o-phenylenediamine which subsequently underwent cyclization in the presence of CO_2 and H_2. Heterogeneously catalyzed methods also suffer from low catalyst stability or high loadings of metals [19]. Thus, designing low metal loaded catalysts will add to the advantages of the existing methodologies in the synthesis of benzimidazole derivatives. In another study, Dutta et al., showed remarkable catalytic activity for the synthesis of benzimidazole derivatives under mild conditions using organic–inorganic hybrid porous iron–phosphonate material which contained both microspores and mesoporous and a high Fe loading (26.7wt%) [20].

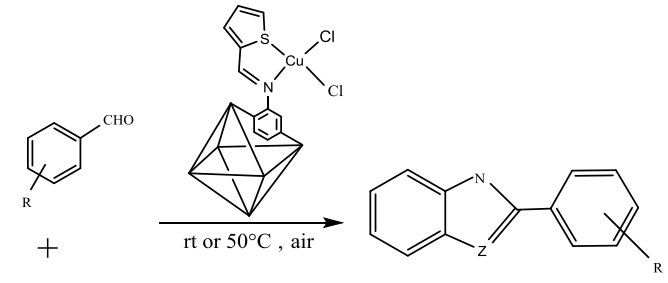
Abstracts

(A) Najari et al (2019) used a zirconium-based UiO-66-NH_2 metal–organic framework (MOF) reformed by melamine (Mlm) to support CuO nanoparticles (NPs). In fact, Melamine was used as a platform yielding the uniform, homogeneous distributed NPs on the surface of the frameworks and creating a strong bonding to the NPs which prevented undesirable leaching. The researchers used UiO-66-NH_2-Mlm/CuO NPs in the Buchwald–Hartwig C–N cross-coupling reaction for arylated anilines synthesis from phenyl iodide, bromide, and chloride and primary and secondary amines in DMF at 110°C. They also used a recyclable and reusable catalyst, which revealed good stability in reactions, in order to synthesize benzimidazole derivatives substituted via various aromatic aldehydes and o-phenylenediamine in the absence of an oxidant in EtOH at 25°C. [21].

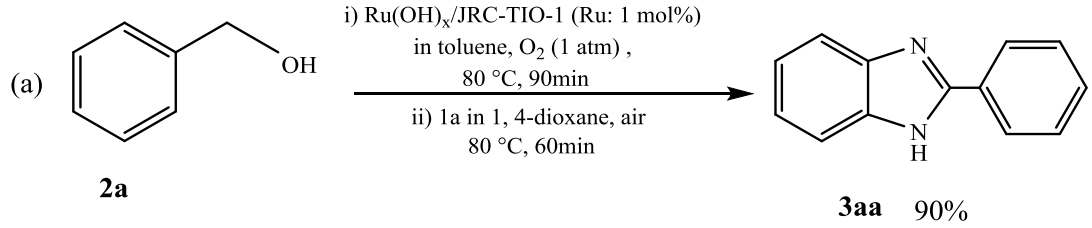


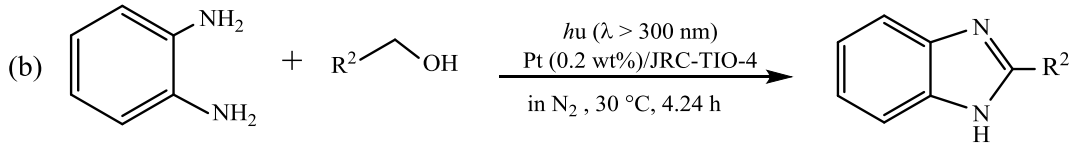
UiO-66-NH_2 UiO-66-NH_2-Mim UiO-66-NH_2-Mim/CuO

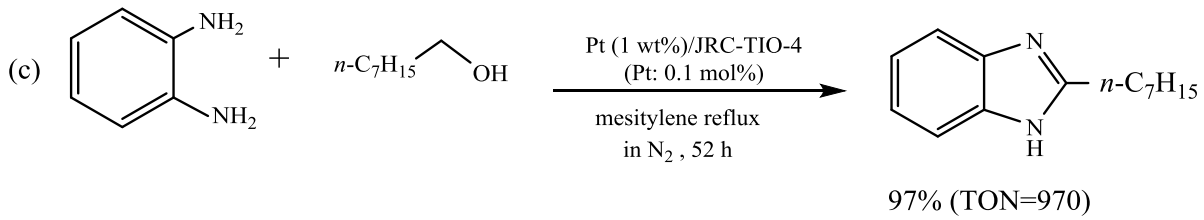
(B) In their study on the anchoring of Cu (II), as the catalyst, onto UiO-66-NH_2 metal−organic framework, in 2015, Kardanpour et al. reported an efficient method for benzimidazoles and benzothiazoles synthesis at room temperature. In this method, the synthesis is carried out, first, by the modification of the aminated UiO-66 with thiophene-2-carbaldehyde and, second, the reaction of the Schiff base prepared by $CuCl_2$. Following these stages, the reaction of aldehydes with 1,2-diaminobenzene or 2-aminothiophenol and UiO-66-NH_2-TC-Cu, a high quality catalyst, led to the synthesis of benzimidazole and benzothiazole derivatives. The Cu (II)-containing MOF showed excellent recyclability since it could be used for several times with no substantial loss of its activity [22].



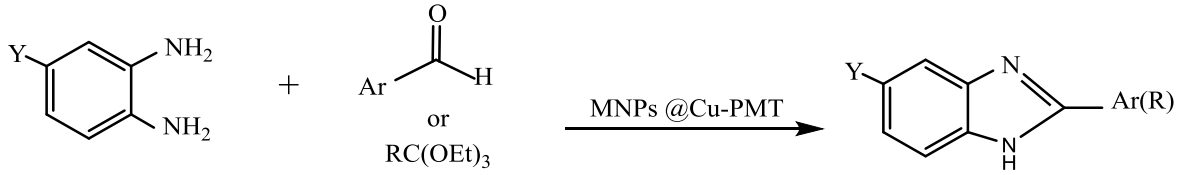
(C) In a review, Wada et al. (2019) briefly summarized the reaction of the primary alcohols and 1,2-phenylenediamine derivatives along with titania-supported iridium catalysts which resulted in the dehydrogenative synthesis of benzimidazoles. Their review was indicative of high-quality activities of titania-supported iridium catalysts in 25°C. Titania supports were shown to affect the iridium catalyst activity under low temperatures, i.e., at 100 °C, but with the existence of titania-supported rutile catalysts, the reaction of 1,2-phenylenediamine and benzyl alcohol proceeded smoothly to give 2-phenylbenzimidazole with high yields (up to 88%). Catalysts supported on anatase were also shown to be of poor activity at 100 °C. Based on the findings, CO uptake was positively related to titania-supported catalysts activity. That is, when well-reduced iridium species was applied on rutile, a significant catalytic activity occurred. As the results, the study suggests that the selection of proper titania-supported iridium catalysts be essential [23].



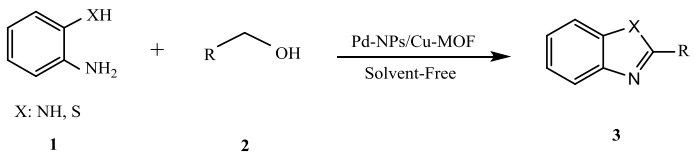




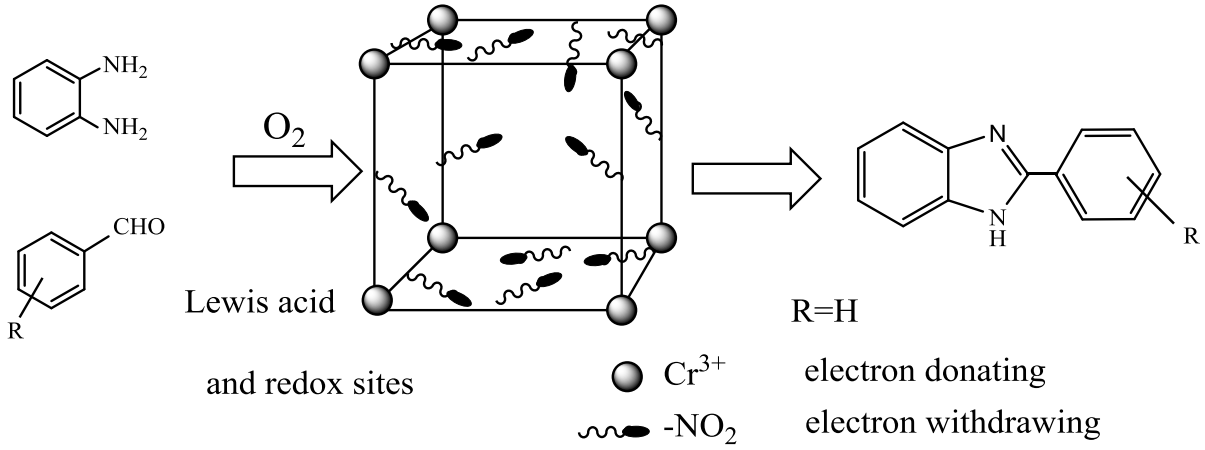
(D) In 2017, Mobini khaledi et al presented a new separable and reusable heterogeneous catalyst, i.e., magnetic mesoporous poly (melamine-terphthaldehyde) nanocomposite containing copper ions (MNPs@Cu-PMT), which proved to be highly efficient and stable for benzimidazoles synthesis [24].



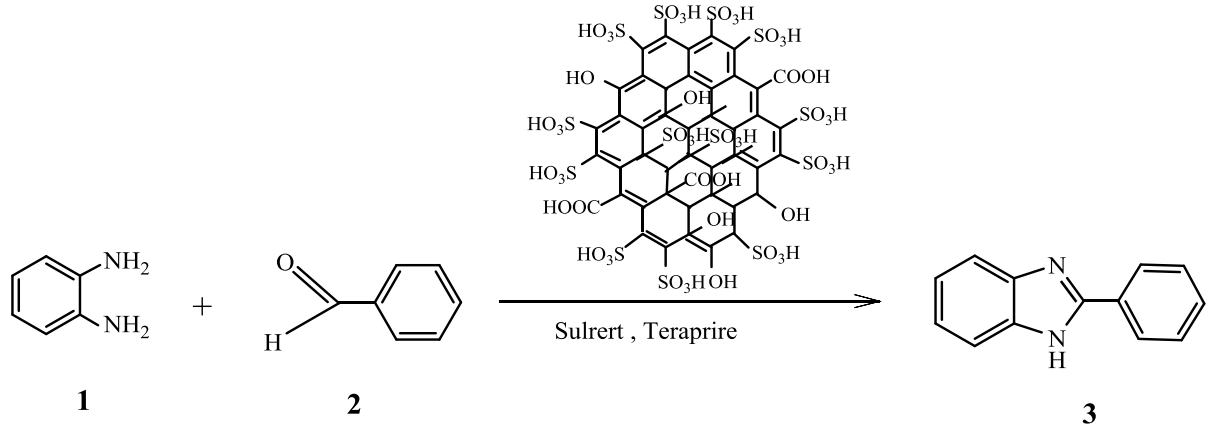
(E) Another efficient synthetic approach was presented by Mokhtari and Bozcheloei (2018) to form a wide range of benzoazoles through dehydrogenative coupling of 1,2-phenylenediamine or 2-aminothiophenol and benzyl alcohols under solvent-free condition by a new heterogeneous catalyst, i.e., $Pd/Cu_2(BDC)_2(DABCO)$-MOF. The catalyst exhibited excellent recyclability (reused 4 times) with no loss of efficiency [25].



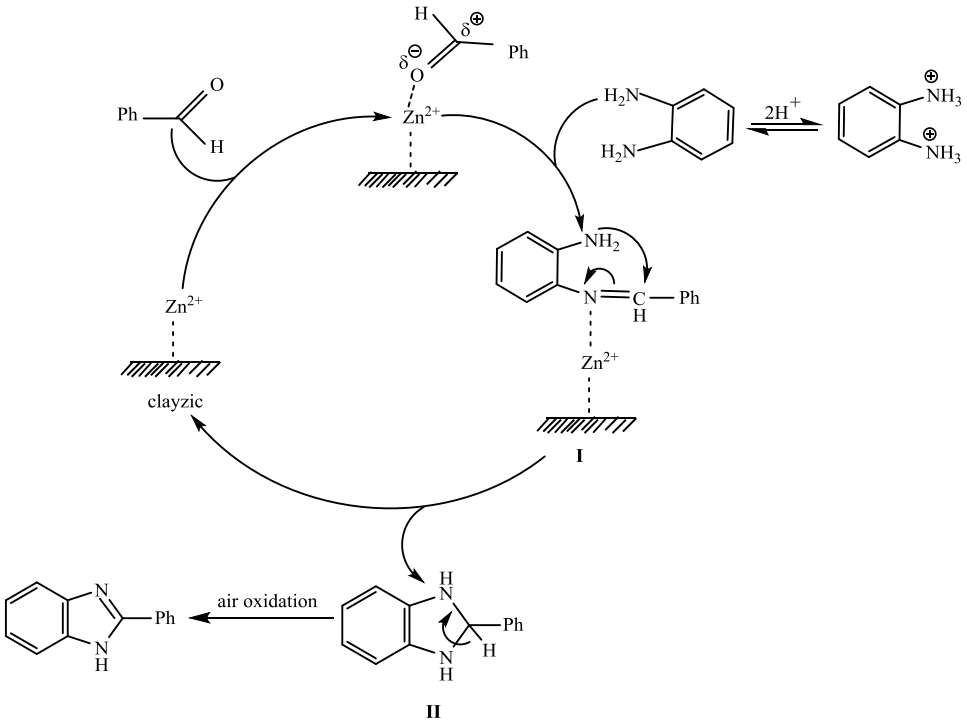
(F) In 2020, Vallés-García et al. presented MIL-101(Cr)-NO_2 metal organic framework and examined its performance as a heterogeneous bi-functional catalyst (acid and redox) by catalyzed condensation on acid sites and subsequent oxidation dehydrogenation. MIL-101(Cr)-NO_2 could be reused five times with no loss in its efficiency [26].



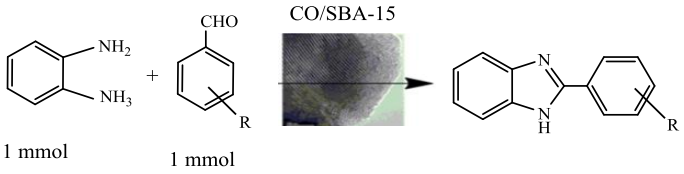
(G) In another study, Swami1 et al. (2016) used sulfonated graphene oxide (GO-HSO_3) heterogeneous catalyst to synthesize benzimidazole which was achieved by diamine and aldehyde reaction at room temperature under solvent free conditions. A selective synthesis of benzimidazole, GO-HSO_3 showed excellent activity. That is, by the use of 0.1 mg of the catalyst, 100 % conversion of reactants and up to 89.0 % yield of respective benzimidazole were obtained in very short reaction time. The separation of the GO-HSO_3 catalyst from the reaction yield was carried out ultimately through a simple filtration process. Interestingly, the catalyst could be used several times with no noticeable loss of its activity and selectivity. High performance, low cost, easy work-up procedure, short reaction time, and solvent free condition are among the strengths of this protocol. The results of their study were indicative of eco-friendliness, high efficiency, and high yield of the proposed method for benzimidazole derivatives synthesis at 25 °C [27].



(H) A very convenient, green, atom-economical, and efficient protocol was presented by Dhakshinamoorthy et al (2011) where clayzic was used in aqueous media at 25 ° C in carbonyl compounds and o-phenylenediamine to synthesize various benzimidazoles and quinoxalines. In contrast to the various catalysts (including claycop and Zn^{2+}–Y) examined in the study, clayzic led to higher yields of benzimidazoles and quinoxalines. Although this method failed to prepare imidazoline with a flexible diamine like ethylenediamine, a bis-Schiff base was formed. Milder conditions, absence of coupling agents, and no wastes were among other significant features of this protocols [28].



(I) Rajabi et al. (2015) developed a green approach which used oxidative condensation of aromatic aldehydes with o-phenylenediamines in the presence of cobalt (II), which was supported on mesoporous silica-type material, for the one-pot synthesis of benzimidazole derivatives. [29]. The researchers were able to recover the supported cobalt catalyst after the completion of reaction completion and recycle it for seven times with an excellent durability and no significant loss in efficiency.



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