Iranian Journal of Catalysis Spotlight 8(2), 2018, 151-154

IRANIAN JOURNAL OF CATALYSIS

Imidazolium-based salts: With Y-aromatic counterions

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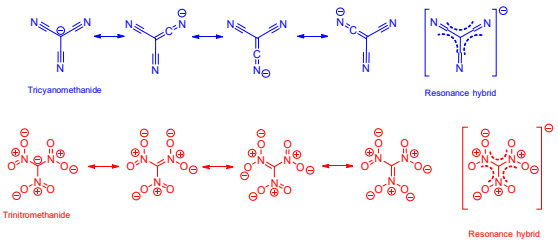
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

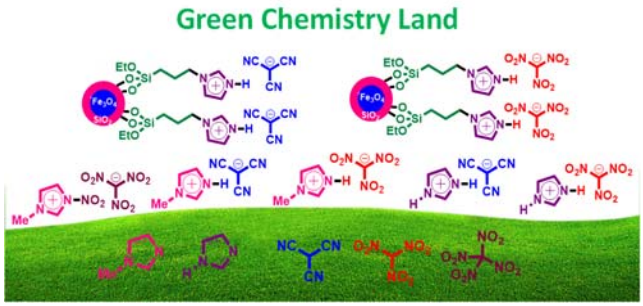
Ionic liquids and molten salts have privileged position in the chemistry and chemical industries. These versatile structures represent varied distinct traits such as insignificant vapor pressure, large temperature window of molten state and unique solvation characteristics [1]. Therefore, exploring, designing and presenting new ionic liquids and molten salts using specific counterions are highly valuable. Among applied counterions, tricyanomethanide and trinitromethanide are quite unique. For example, energetic organic salts were synthesized by using trinitromethanide counterion [2,3]. These anions stabilized by concept of Y-aromaticity (Scheme 1).



Scheme 1. Stability of tricyanomethanide and trinitromethanide due to existence of Y-aromaticity.

Y-aromaticity exists in Y-shape and planar molecules, ions and/or intermediate bearing resonance groups such as guanidine and guanidinium cations [4-8].

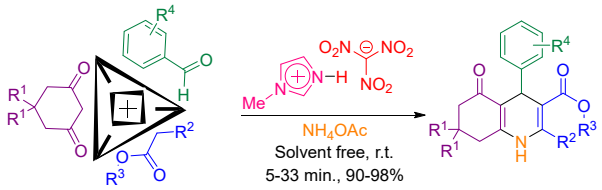
In this spotlight, an attempt has been made to highlight the recent versatilities of tricyanomethane, trinitromethane and tetranitromethane as unique potential structures for construction of imidazolium-based salts which have been used as catalysts (Scheme 2). Also, the capability of the prepared imidazolium-based nano and nanomagnetic catalysts for the synthesis of fascinating heterocyclic molecules were reported.



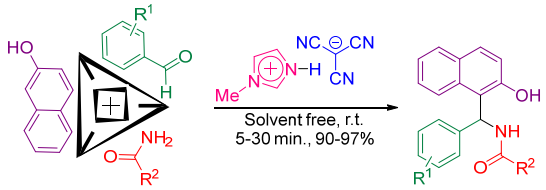
Scheme 2. Unique imidazolium-based nano and nanomagnetic catalysts.

Abstracts

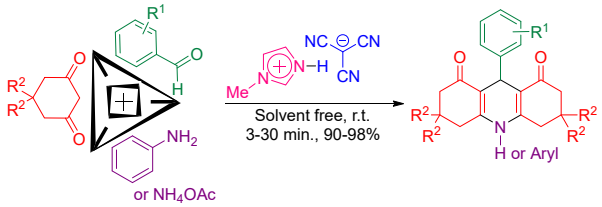
(A) In 2014, Zolfigol and co-workers, present the first nano ionic liquid namely 1-methylimidazolium trinitromethanide {[HMIM]C$(NO_2)_3$} by the reaction of 1-methyl imidazole and trinitromethane. The synthesized nano ionic liquid, represents elegant catalytic behavior towards the Hanztsch four-component condensation reaction [9].



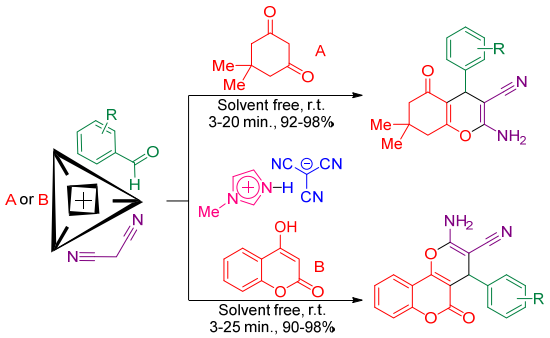
(B) In 2015 the first nanostructured molten salt namely 1-methylimidazolium tricyanomethanide {[HMIM]C$(CN)_3$} was reported. Experimental data revealed that {[HMIM]C$(CN)_3$} acts as powerful catalyst for the synthesis of 1-amidoalkyl-2-naphthols at room temperature under solvent free conditions [10].



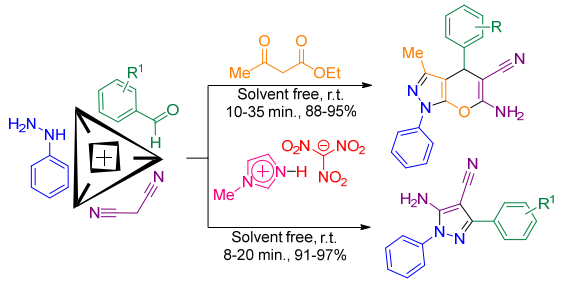
(C) In another investigation, {[HMIM]C$(CN)_3$} applied as nanostructured molten salt catalyst for the preparation of 1,8-dioxodecahydroacridine derivatives through a one-pot condensation reaction between cyclic 1,3-diketone, aldehydes and various anilines or ammoniumacetate as nitrogen source [11].



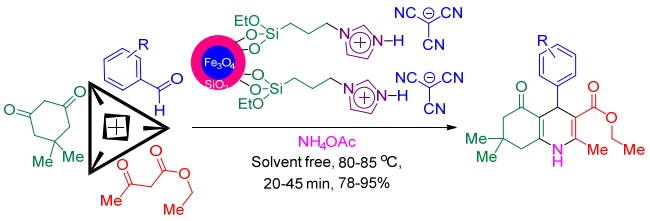
(D) In continued, {[HMIM]C$(CN)_3$} has been used as a powerful catalyst for simple and rapid preparation of tetrahydrobenzo[*b*]pyrans and 3,4 dihydropyrano[*c*]chromene derivatives at room temperature under solvent-free conditions [12].



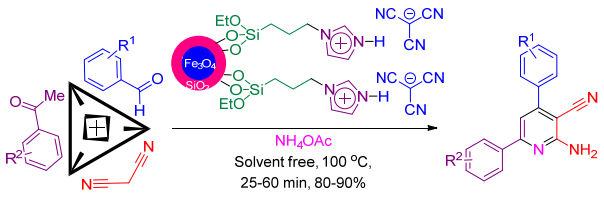
(E) In another study, {[HMIM]C$(NO_2)_3$} applied as nano ionic liquid catalyst for the preparation of pyrazole derivatives under green conditions [13]. In this exploration it is demonstrated that the final step of the mechanistic process for the synthesis of 5-amino-pyrazole-4-carbonitrile derivatives proceeds *via* an anomeric-based oxidation mechanism [14-17].



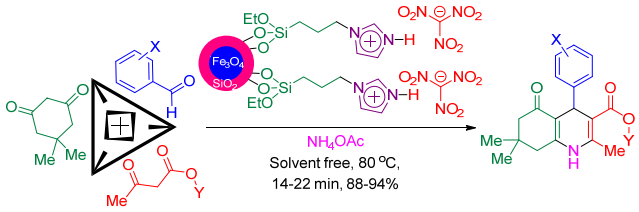
(F) A novel silica-coated magnetic nanoparticle immobilized ionic liquid namely {Fe_3O_4@SiO_2@$(CH_2)_3$Im}C$(CN)_3$ was designed, synthesized and fully characterized. The constructed imidazolium-based nanomagnetic catalyst shows elegant catalytic application at the synthesis of polyhydroquinoline derivatives. Also, the catalyst represents great potential of recycling and reusing capability [18].



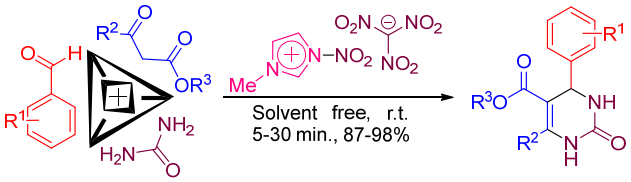
(G) {Fe_3O_4@SiO_2@$(CH_2)_3$Im}$C(CN)_3$ has been also applied as an ionically tagged nanostructured catalyst for the synthesis of 2-amino-4,6-diphenylnicotinonitriles. A good range of aromatic aldehydes were reacted with acetophenone derivatives, malononitrile and ammonium acetate to furnished desired 2-amino-4,6-diphenylnicotinonitrile derivatives via an anomeric-based oxidation mechanism [19].



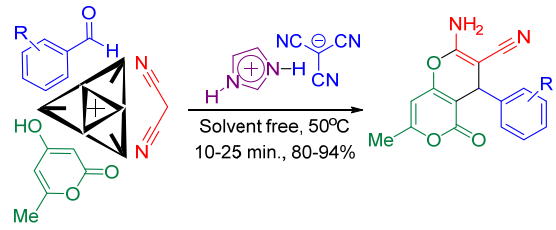
(H) In another investigation, {Fe_3O_4@SiO_2@$(CH_2)_3$Im}$C(NO_2)_3$ as a novel heterogeneous reusable catalyst was designed, synthesized and fully characterized. The resulting nanomagnetic core-shell catalyst was successfully applied for the preparation of polyhydroquinolines from the reaction of aryl aldehydes, dimedone, ethyl acetoacetate or methyl acetoacetate and ammonium acetate as a nitrogen source under green conditions [20].



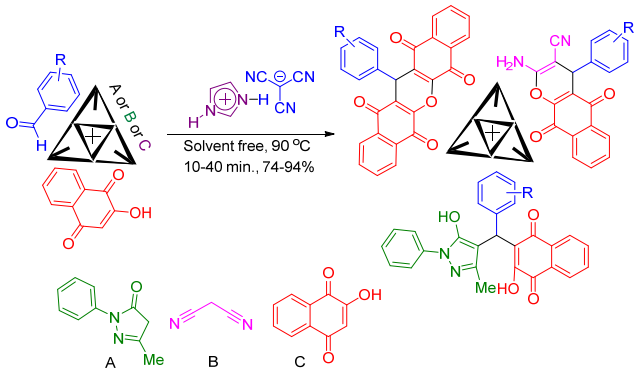
(I) A unique green and nano structured ionic liquid based on tetranitromethane namely {[MIM-NO_2]$C(NO_2)_3$} illustrates brilliant catalytic performance towards the synthesis of novel Biginelli-type compounds from the reaction between aromatic aldehydes, urea and 1,3-dione derivatives at room temperature and under solvent-free conditions [21].



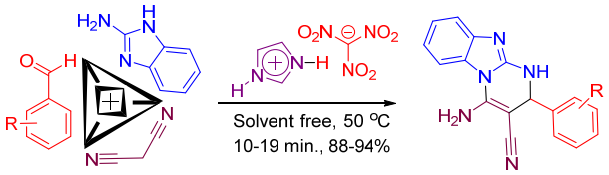
(J) 1*H*-Imidazol-3-ium tricyanomethanide {[HIM]$C(CN)_3$} as a novel nanostructured molten salt was synthesized. The catalytic activity of {[HIMI]$C(CN)_3$} has been successfully tested in a three-component domino condensation reaction. A good scope of pyrano[4,3-*b*]pyran derivatives were prepared under solvent free condition at 50 °C [22].



(K) In another protocol, {[HIM]$C(CN)_3$} present robust catalytic applicability for the construction of biological naphthoquinone-based compounds under mild and green reaction conditions. A wide range of aromatic aldehydes subjected to react with 2-hydroxynaphthalene-1,4-dione and 3- methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one or malononitrile to yield desired biological-based molecules in short reaction time with high to excellent yields [23].



(L) In a separate investigation, 1*H*-imidazol-3-ium trinitromethanide {[HIMI]C(NO_2)$_3$} as a green and nano sized ionic liquid catalyst was reported. The prepared catalyst, furnished imidazo[1,2-*a*]pyrimidine-3-carbonitrile derivatives under mild reaction conditions [24].



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