

Organic salts: With Y-aromatic counterions (Part II)

Compiled by Meysam Yarie

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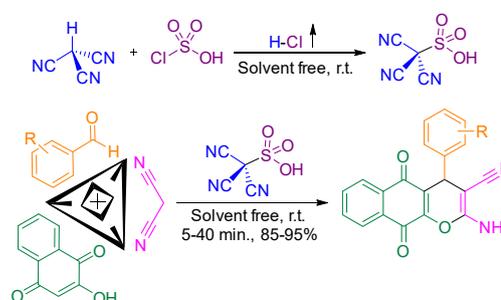
This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Y-conjugated structures such as nitrate or tricyanomethanide and dendritic anions such as trinitromethanide and hexanitroisobutene dianion $[(C_4(NO_2)_6)^{2-}]$ salts have found an influential position in both natural and industrial chemical processes. Among these structures, tricyanomethanide and trinitromethanide are highly regarded. Tricyanomethanide and trinitromethanide are conjugated bases of tricyanomethane and trinitromethane which are highly acidic. Deprotonation of tricyanomethane ($pK_a = -5$) and trinitromethane ($pK_a = 0$), generates two anions which are impressively stabilized by the concept of Y-aromaticity (Scheme 1) [1-3]. These anions are adaptable with various purposes in chemical and industrial processes [4-8]. Recently, a novel and unique nanostructured solid acid, namely tricyano methanesulfonic acid (TCMS), has been synthesized and used as an ecofriendly and reusable catalyst for synthesis of 2-amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4H-benzo[g]chromenes (Scheme 2) [8]. Very recently, imidazolium-based salts with Y-aromatic counterions were reviewed [9].



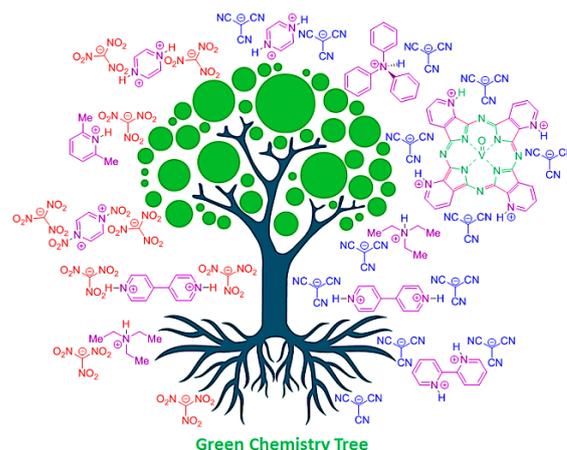
Scheme 1. Y-Aromaticity in tricyanomethanide and trinitromethanide anions.



Scheme 2. Synthesis of TCMS and its application towards the synthesis of chromenes.

On the other hands, due to the several influential characteristic such as minor vapor pressure, excellent solvation properties and broad range of ionic liquids and molten salts, emerged as an interdisciplinary filed. Also, they can be applied for different goals in laboratory and industrial chemical processes [10,11].

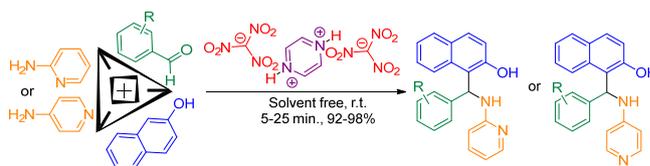
This spotlight highlighted the recent investigation towards the synthesis of novel ionic liquids and molten salts based on tricyanomethanide and trinitromethanide as Y-aromatic counterions and their application at the multicomponent synthesis of various heterocyclic molecules (Scheme 3).



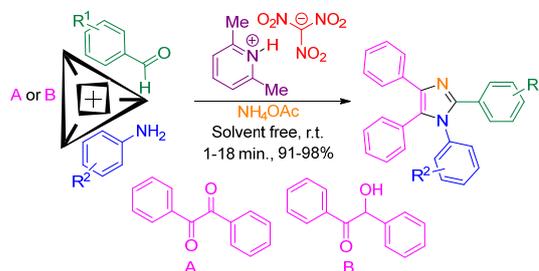
Scheme 3. Ionic liquids and molten salts based on tricyanomethanide and trinitromethanide as Y-aromatic counterions.

Abstracts

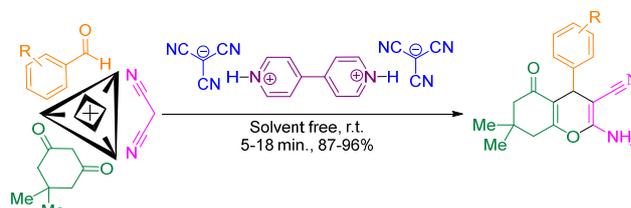
(A) In 2015, Zolfigol and co-workers, reported the synthesis and characterization of pyrazine-1,4-dium trinitromethanide $\{[1,4\text{-DHPyrazine}][\text{C}(\text{NO}_2)_3]_2\}$ as a novel nanosized molten salt. $\{[1,4\text{-DHPyrazine}][\text{C}(\text{NO}_2)_3]_2\}$ represent elegant catalytic performance at the synthesis of 1-(α -aminoalkyl)-2-naphthol derivatives [12].



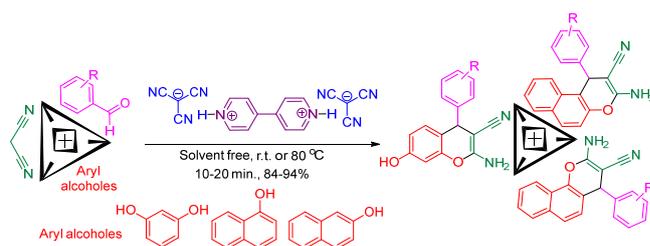
(B) In another study, 2,6-Dimethylpyridinium trinitromethanide $\{[2,6\text{-DMPyH}][\text{C}(\text{NO}_2)_3]\}$, was designed, synthesized and fully characterized. The resulting nanosized molten salt, efficiently catalyzed the reaction of benzil/benzoin, aldehyde derivatives, amines and ammonium acetate towards the preparation of 1,2,4,5 tetrasubstituted imidazole derivatives by a one-pot four component condensation reaction [13].



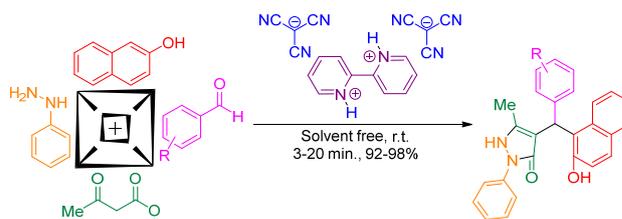
(C) Through a brilliant protocol, tetrahydrobenzo[*b*]pyrans derivatives were synthesized under green conditions in the present of [4,4'-bipyridine]-1,1'-dium tricyanomethanide $\{[4,4'\text{-BPyH}][\text{C}(\text{CN})_3]_2\}$ as a recoverable catalyst. Also, $\{[4,4'\text{-BPyH}][\text{C}(\text{CN})_3]_2\}$ was applied as a catalyst for the facile preparation of amido and aminoalkyl naphthol derivatives [14].



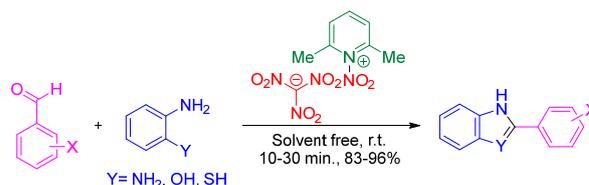
(D) In continued, the same team applied $\{[4,4'\text{-BPyH}][\text{C}(\text{CN})_3]_2\}$ as a bifunctional nanostructured molten salt catalyst for the facile preparation of 2-amino-4*H*-chromene derivatives through the reaction of varied aromatic aldehydes with malononitrile and resorcinol, 1-naphthol or 2-naphthol under mild and green reaction conditions [15].



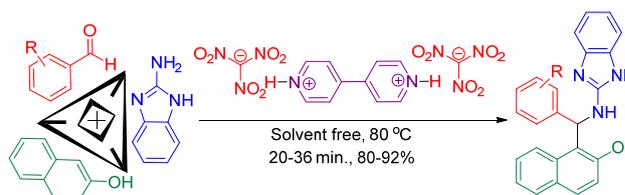
(E) In another study, [2,2'-Bipyridine]-1,1'-dium tricyanomethanide $\{[2,2'\text{-BPyH}][\text{C}(\text{CN})_3]_2\}$ was prepared and fully characterized using required techniques. Afterwards, this bifunctional nanostructured ionic liquid successfully applied as catalyst for the synthesis of 2-aryl-5-methyl-2,3-dihydro-1*H*-3-pyrazolones through a condensation reaction between aromatic aldehydes, ethyl acetoacetate, phenyl hydrazine, and β -naphthol under benign conditions [16].



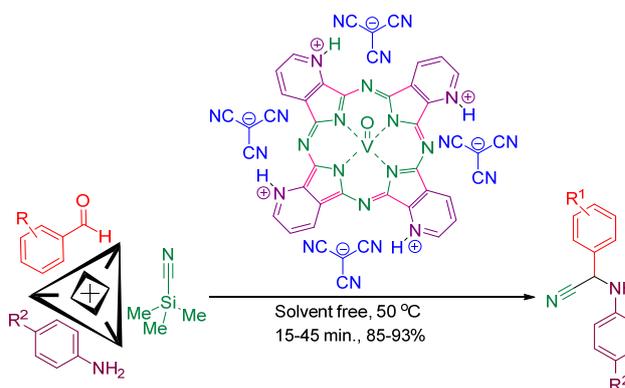
(F) In a separate study, a nanostructured molten salt, namely 2,6-dimethyl-1-nitropyridin-1-ium trinitromethanide $[2,6\text{-DMPy-NO}_2][\text{C}(\text{NO}_2)_3]$ was reported by Zolfigol and co-workers. $[2,6\text{-DMPy-NO}_2][\text{C}(\text{NO}_2)_3]$ represent powerful catalytic performance at the synthesis of 2-substituted benz-(imida, oxa and othia)-zoles [17]. Experimental and theoretical investigations approved the synthesis of target molecules through an anomeric based oxidation mechanism [18-20].



(G) In 2017, [4,4'-bipyridine]-1,1'-dium trinitromethanide was reported as a novel nanosized bifunctional ionic liquid. After structural verification of the titled molecule, its elegant catalytic activity was demonstrated at the synthesis of 1-(benzoimidazolylamino)methyl-2-naphthol derivatives *via* a straightforward one-pot three-component condensation reaction [21].



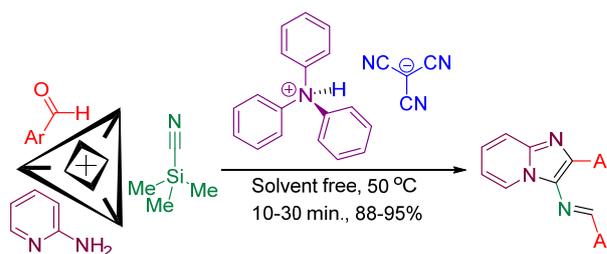
(H) In another exploration, a vanadium surface-free phthalocyanine-based molten salt namely, tetra-2,3-pyridiniumporphyrinato-oxovanadium tricyanomethanide, $\{[\text{VO}(\text{TPPA})][\text{C}(\text{CN})_3]_4\}$, was reported as a nano catalyst for the Strecker synthesis of α -aminonitrile derivatives. One of the main merits of the $\{[\text{VO}(\text{TPPA})][\text{C}(\text{CN})_3]_4\}$, is the simplicity of the recovering and reusing in its catalytic cycle [22].



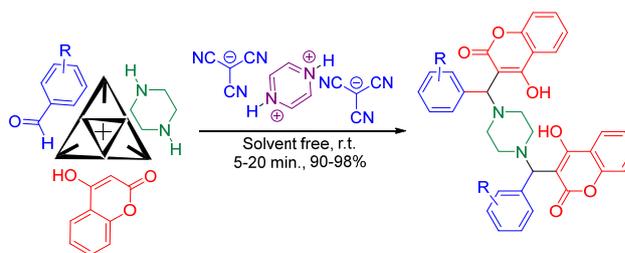
(I) Synthesized triethylammonium-based ionic liquid and molten salt represent excellent catalytic performance towards the preparation of 2-amino-4-aryl-6-(arylamino)pyridine-3,5-dicarbonitrile derivatives through an one-pot three-component protocol between a good range of aromatic aldehyde, malononitrile and aniline derivatives [23] *via* an anomeric-based oxidation process [18-20].



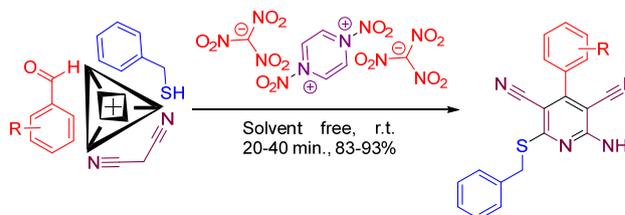
(J) An ammonium-based nanostructured molten salt namely triphenylammonium tricyanomethanide was developed by Zolfigol and co-workers. The resulting structure efficiently catalyzed *N*-benzylidene-2-arylimidazo[1,2-*a*]pyridin-3-amine derivatives. The nanosized catalyst exhibit high potential of recycling and reusing in the described reaction [24].



(K) In another assay, a new nano molten salt based on tricyanomethanide anion entitled pyrazine-1,4-dium tricyanomethanide {[1,4-DHPyrazine][C(CN)₃]₂} was synthesized and characterized. {[1,4-DHPyrazine][C(CN)₃]₂} was applied as robust catalyst at the synthesis of novel piperazine based bis(4-hydroxy-2*H*-chromen-2-one) derivatives in short reaction times and high yields [25].



(L) 1,4-Dinitropyrazine-1,4-dium trinitromethanide {[1,4-pyrazine-NO₂][C(NO₂)₃]₂} as a novel nanostructured molten salt was synthesized. Also, its catalytic performance was probed towards the synthesis of 2-amino-3,5-dicarbonitrile-6-sulfanylpyridine derivatives through the reaction of aromatic aldehydes, malononitrile and benzyl mercaptan [26]. Experimentally and theoretically demonstrated that the final step of the reaction proceeds via an anomeric-based oxidation mechanism [18-20].



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