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A Review of Catalytic Innovations in the Synthesis of 1, 4-Dihydropyrano [2, 3-C] Pyrazoles via Four Component Method in the Last Decade

Amit S. Waghmare
Department of Chemistry, ACS College, Satral, Ahilyanagar 413711, Maahrashtra, India

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ABSTRACT

1,4-Dihydro Pyrano [2,3-c]pyrazole (1,4-DHPP) derivatives have many biological and medicinal properties hence received an interest by organic and medicinal chemists. Now a days multi-component reactions (MCRs) have been adopted for the synthesis of highly functionalized 1,4-dihydro pyrano[2,3-c] pyrazole derivatives as MCRs have its own importance in the field of chemistry and environment. .

This review gives detail information about the methods used to synthesize 1,4-Dihydro Pyrano [2,3-c]pyrazole derivatives by one-pot four components over the last ten years. As compared with two components and three component methods four component condensation method is used in the greater extent by the researchers. This review also gives information about the different catalytic techniques and methods use for the synthesis of 1,4-DHPP.

Keywords: Pyrano[2,3-c]pyrazole, four-component reaction, ethyl acetoacetate, one-pot synthesis.

I. INTRODUCTION

The multi-component reactions (MCRs) have emerged as a great tool for synthetic transformations due to its operational simplicity, less hazardous and minimum side products with higher yields of desired products. It has advantages over the multi-step reactions in comparison with experimental procedures, the yield of the desired products, time of the reactions, isolation of any intermediate compound, which saves time, energy and raw materials required for the reaction, making the protocol economically attractive and environmentally friendly [1].

In recent years, 1,4-Dihydro Pyrano [2,3-*c*]pyrazole attracted a great importance due to its biological and pharmaceutical activities [3]. In the literature several 1,4-Dihydro Pyrano [2,3-*c*]pyrazole derivatives were reported which shows various important biological activities such as analgesic [4], anti-inflammatory [5], anti-bacterial [6], anti-microbial [7] and anti-tubercular [8].

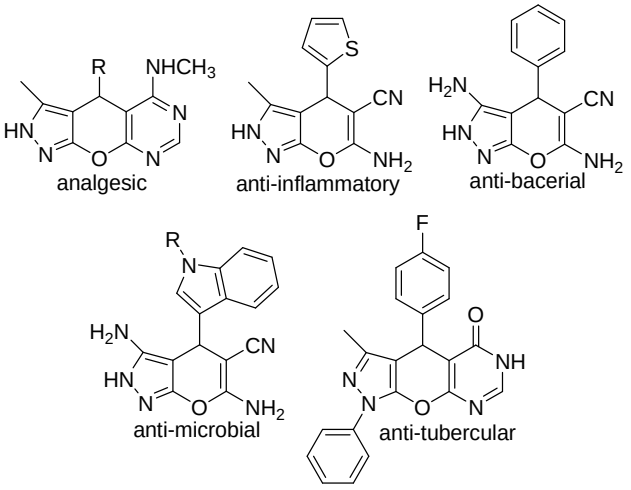
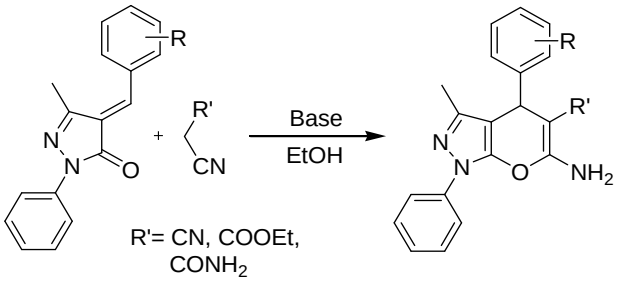


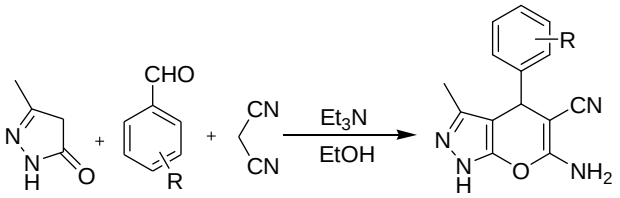
Figure 1 Examples of biologically active pyranopyrazole analogs

Junek and Aigner for the first time reported the synthesis of pyrano-pyrazole from methyl-1-phenylpyrazolin-5-one and tetracyanoethylene [9]. Synthesis of 4*H*-pyrano-[2,3-*c*]-pyrazole was reported by H. H. Otto in 1974 by addition of malononitrile to arylidene-3-methyl-2-pyrazolin-5-one (Scheme 1) [10].



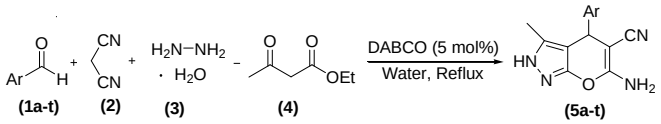
Scheme 1

Three component condensations for the development of pyranopyrazoles were achieved first time by Sharanin et al. (Scheme 2) [11]. This protocol was achieved by triethylamine as a catalyst in ethanol from aldehyde, malononitrile and 3-methyl-5-pyrazolone.



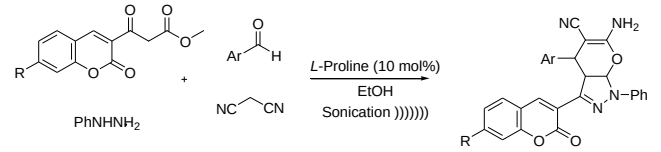
Scheme 2

Waghmare and Pandit reported the synthesis of 1,4-dihydropyrano [2,3-*c*] pyrazole derivatives using DABCO in aqueous media (Scheme 3) [12].



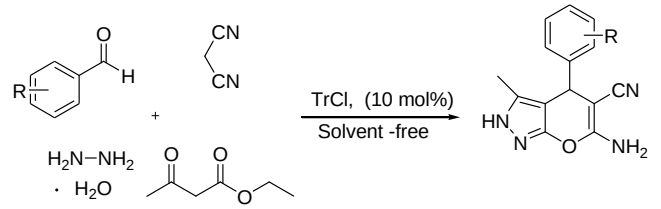
Scheme 3

Synthesis of coumarin-c ontaining dihydropyrano[2,3-*c*]pyrazoles under ultrasonic irradiation is achieved by Seydiment et al. catalyzed by L-proline using condensation of aromatic aldehydes, malononitrile, phenyl hydrazine and β-dicarbonyl compound (Scheme 4) [13].



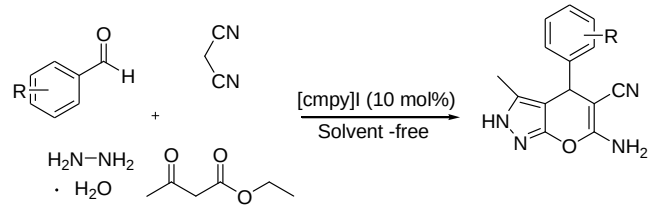
Scheme 4

Moosavi-Zare et al. used trityl cabocation mediated synthesis of pyranopyrazole derivatives from aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate under solvent free condition (Scheme 5) [14].



Scheme 5

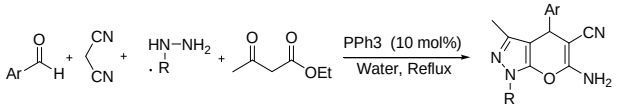
1-(carboxymethyl)-pyridinium iodide on the synthesis of pyranopyrazole derivatives were synthesized under solvent free conditions by Moosavi-Zare et al. by condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 6) [15].



Scheme 6

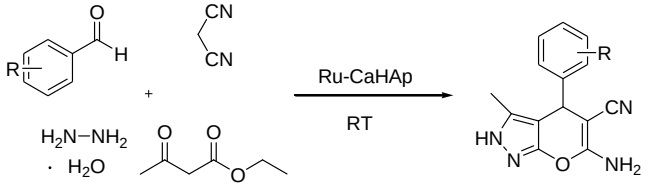
Four component condensation of hydrazine hydrate, ethylacetoacetae, various aldehydes and malononitrile in the presence of triphenyl phosphine in various

concentrations and different solvents were carried out by I.A. Khodja et al. (Scheme 7) [16]



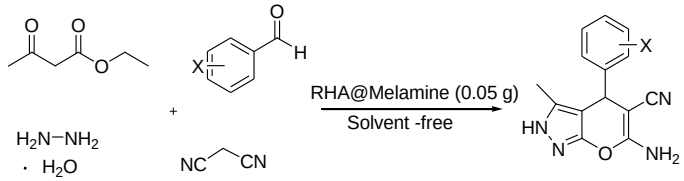
Scheme 7

Narayana et al. carried out the synthesis of Pyranopyrazoles by the condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate using Ru-Hydroxyapatite as a reusable catalyst (Scheme 8) [17].



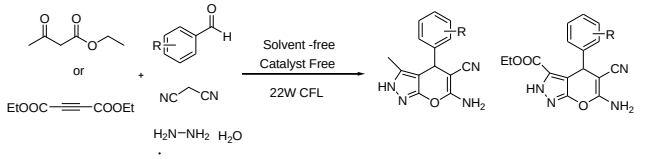
Scheme 8

Solvent free condensations of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate for the synthesis of pyranopyrazole were achieved by Davarpanah and Khoram using RHS@Melamine (Scheme 9) [18].



Scheme 9

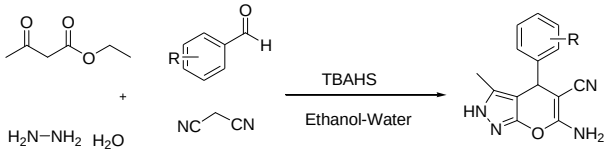
Tripathi et al carried out the synthesis of pyrano[2,3-*c*]pyrazoles from aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate in the presence of light. This method is also explored by using diethyl acetylene dicarboxylate in place of ethylacetoacetate (Scheme 10) [19].



Scheme 10

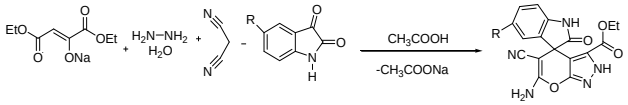
Maddila et al. prepared and used Ceria-doped zirconia used as a catalyst for the synthesis of new pyrano[2,3-*c*]pyrazoles derivatives for the condensation reaction of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate [20].

A green and efficient method as developed by Bhosale et al. synthesis of pyranopyrazole derivatives using tetrabutyl ammonium hydrogen sulphate for the synthesis of pyranopyrazole derivatives by condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 11) [21].



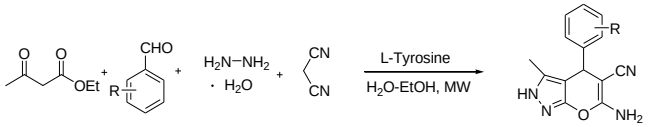
Scheme 11

Synthesis of ethyl 6-amino-5”-cyano-2-oxo-2” H-spiro[indoline-3,4’-pyrano[2,3-*c*] pyrazole]-3”-carboxylates were carried out by condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate by Gein et al. using sodium acetate in acetic acid (Scheme 12) [22].



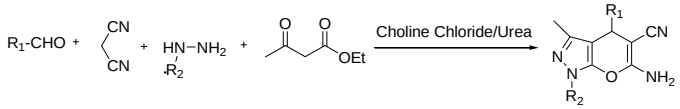
Scheme 12

Microwave irradiation technique is used for the efficient synthesis of dihydropyrano[2,3-*c*]pyrazoles using L-tyrosine as a catalyst for the condensation of various aldehydes, aceto acetic esters, malononitrile and hydrazine hydrate (Scheme 13) [23].



Scheme 13

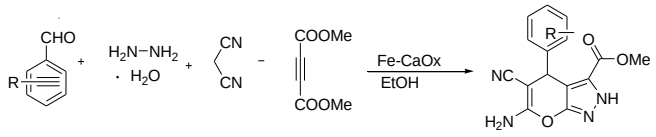
New 6-amino-4-aryl-2,4-dihydro-3-phenyl pyrano[2,3-*c*] pyrazole-5-carbonitrile derivatives were synthesized by the condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate using Choline Chloride based thoiurea as a catalyst (Scheme 14) [24].



Scheme 14

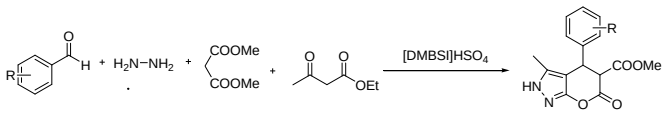
Synthesis of pyranopyrazoles were carried out by Gangu et al. using aldehydes, malononitrile, hydrazine hydrate and dimethyl acetylene dicarboxylaate by

iorn doped calcium oxalates as promising heterogeneous catalyst (Scheme 15) [25].



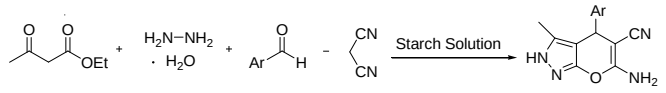
Scheme 15

Farokhian et al. carried out the synthesis of novel pyrano[2,3-*c*]pyrazoles and bis- pyrano[2,3-*c*]pyrazoles under solvent free conditions using sulfonic acid-functionalized ionic liquid from condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 16) [26].



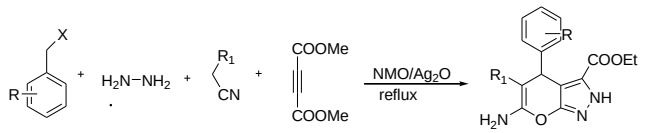
Scheme 16

Starch solution as an nontoxic biodegradable catalyst as used by Vekariya et al. for the synthesis of 6-amino 1,4-dihydropyrano[2,3-*c*]pyrazole-5-c arbonitrile derivatives using aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 17) [27].



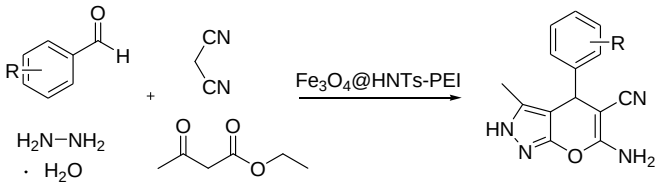
Scheme 17

N-methylmorpholine N-oxide and silver oxide catalyzed synthesis of pyranopyrazole is carried out by Beerappa and Shivashankar using benzyl halide, malononitrile hydrazine hydrate and diethylacetylenedicarboxylate (Scheme 18) [28] .



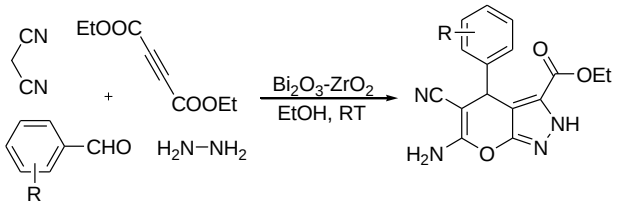
Scheme 18

A new magnetic nanoparticle Fe_3O_4@HNTs-PEI was prepared characterized and used for the synthesis of pyranopyrazole derivatives by Halizadeh and Maleki (Scheme 19) [29].



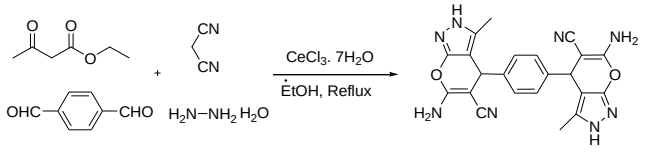
Scheme 19

2,4-dihydropyrano[2,3-*c*] pyrazole-3-carboxylates were synthesized by Bhaskaruni et al. from aldehyde malononitrile, hydrazine hydrate and diethyl acetylenedicarboxylate using bismuth loaded on zirconia as a reusable catalyst (Scheme 20) [30].



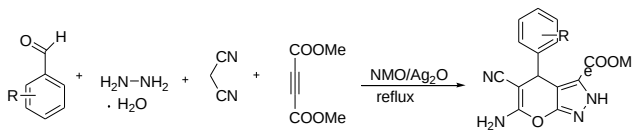
Scheme 20

Singh et al. carried out the synthesis of Bispyranopyrazoles from the aldehyde, hydrazine hydrate, malononitrile and ethyl acetoacetate using cerium chloride in ethanol at reflux condition (Scheme 21) [31].



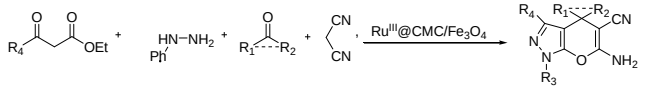
Scheme 21

Ultrasound mediated four component synthesis of pyrano[2,3-*c*] pyrazoles were achieved by Maddila et al. using Mn doped zirconia from aldehyde, hydrazine hydrate, malononitrile and dimethyl acetylenedicarboxylate /ethyl acetoacetate (Scheme 22) [32].



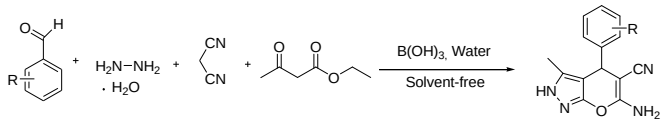
Scheme 22

Chenet al. carried out her synthesis of pyranopyrazole derivatives from the condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate using RuIII@CMC/Fe_3O_4 hybrid catalyst (Scheme 23) [33].



Scheme 23

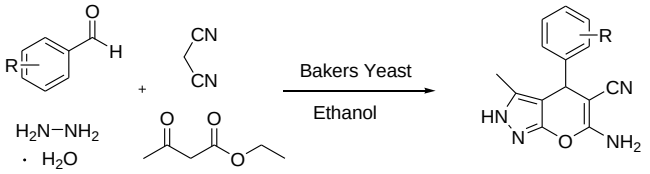
A. R. Moosavi-Zare et al. used aqueous solution of boric acid as an efficient and green catalytic system for the symntesis of pyranopyrazole derivatives by the four component condensation reaction of aryl aldehydes with ethylacetoacetate, malanonitrile and hydrazine hydrate (Scheme 24) [34].



Scheme 24

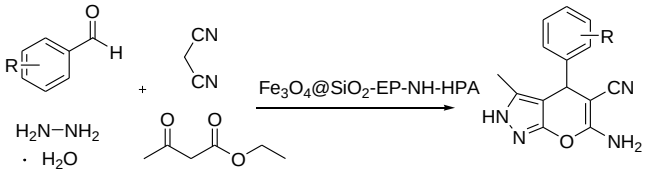
S. Sikandar et al. developed an environmentally benign method for the synthesis of pyrano[2,3-*c*] pyrazole by the condensation of ethyl 3-oxobutanoate, propanedinitrile, hydrazine monohydrate and differen substituted benzaldehyde in the presence of L-cysteine in aqueous ethanol [35].

Bakers yeast as a biocatalyst is used for the synthesis of pyranopyrazoles in etanol using aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 25) [36].



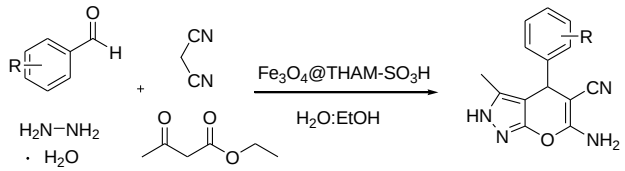
Scheme 25

Novel solid acid nanocatalyst Fe_3O_4@SiO_2-EP-NH-HPA is used for synthesis of pyrano[2,3-*c*] pyrazole derivatives from the condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 26) [37].



Scheme 26

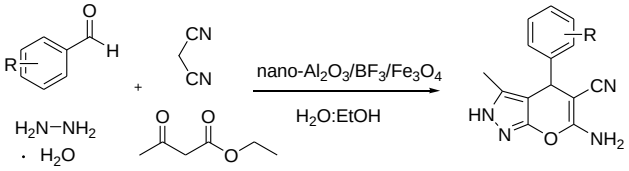
Sulphuric acid on nanoparticles coated with tris (hydroxymethyl) aminomethane was synthesized by Faroughi Niva et al. and used for the synthesis of dihydropyrano[2,3-*c*] pyrazole derivatives (Scheme 27) [38].



Scheme 27

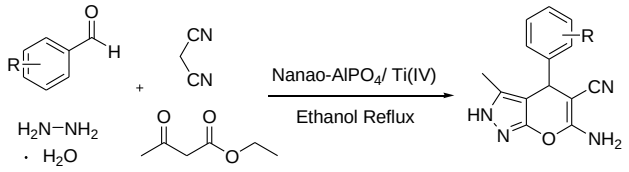
Chattise et al. used Nanostructured zinc as a heterogeneous catalyst for the synthesis of benzoxanthene and pyranopyrazole scaffolds in the presence of aqueous ethanol [39].

Babaei and Mirijalili carried out the synthesis of dihydropyrano[2,3-*c*] pyrazoles via four component condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate using nano-$Al_2O_3/BF_3/Fe_3O_4$ as reusable catalyst (Scheme 28) [40].



Scheme 28

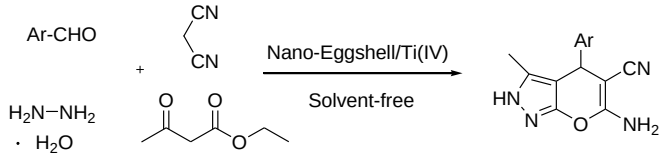
Synthesis of dihydropyrano[2,3-*c*] pyrazoles were achieved by nano-$AlPO_4$/ Ti(IV) as a new and recyclable catalyst by Mehravar et al. using aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate(Scheme 29) [41] .



Scheme 29

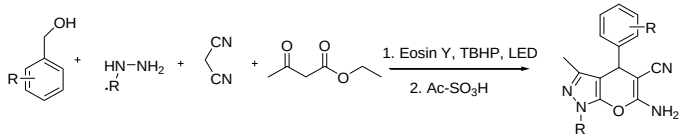
Babaees et al. used metal organic frame work for the synthesis of n-amino-2-pyridone and pyrano[2,3-*c*] pyrazole derivatives via reaction of aldehyde, malononitrile, hydrazine hydrate ethyl cyanoacetate or ethyl acetoacetate [42].

Nano-eggshell/Ti(IV) is used for the synthesis of dihydropyrano[2,3-*c*] pyrazoles using aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate by Tafti et al. (Scheme 30) [43].



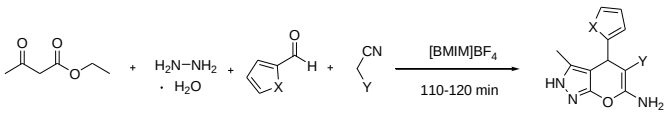
Scheme 30

Nguyen et developed a new pathay for the synthesis of pyrano[2,3-*c*] pyrazoles in the presence of sulphonated amorphous carbon and eosin Y as a catalyst through a four component reaction of benzyl alcohol, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 31) [44] .



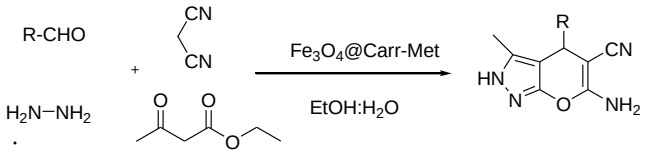
Scheme 31

Synthesis of bioactive pyrano[2,3-*c*] pyrazoles having five membered heterocyclic moiety were achieved by kalpana et al. in the [BMIM]BF_4 as a medium using aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 32) [45] .



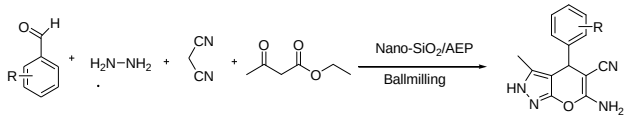
Scheme 32

Heyadri et al. carried out the synthesis of dihydropyrano[2,3-*c*] pyrazoles using a new bio inspired magnetic nanoparticle Fe_3O_4@Carrageenam-Metformin (Scheme 33) [46].



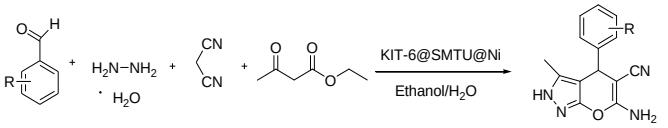
Scheme 33

Nano-silica/aminoethylpiperazine as a metal-free catalyst as used by Mallah and Mirjalili for synthesis of dihydropyrano[2,3-*c*] pyrazoles by ball milling technique (Scheme 34) [47].



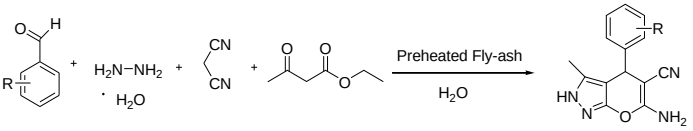
Scheme 34

Ni(II) complex on the surface of mesoporous modified-KIT-6 as a new reusable and highly effficent nanocatalyst were usied by Darabi et al. for the synthesis of pyranopyrazle derivatives in ethanol at reflux condition (Scheme 35) [48].



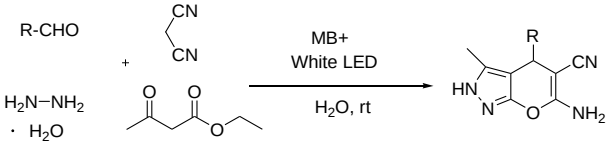
Scheme 35

Fly ash as used for the first time for the synthesis of dihydropyrano[2,3-*c*] pyrazoles from aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate by Pandey et al. (Scheme 36) [49].



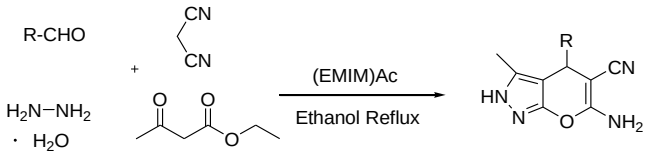
Scheme 36

Methylene blue (MB+) as photo-redox catalyst as used for the synthesis of dihydropyrano[2,3-*c*] pyrazole scaffiold by Mohamadpour et al. by the condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 37) [50].



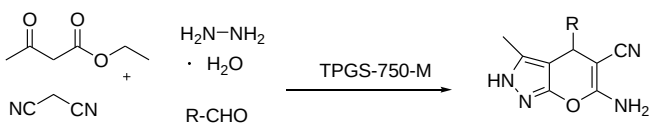
Scheme 37

Pyrano[2,3-*c*] pyrazole derivatives were synhesized by Kataria eta al. using 1-ethyl-3-methylimidazolium acetate as a catalyst via the condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate (Scheme 38) [51].



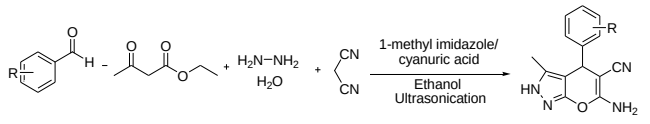
Scheme 38

A. Cetin, M. Y. Bayden, Aqueous TPGS-750-M-mediated synthesis of pyrano[2,3-*c*] pyrazoles: a sustainable and efficient approach. Res. Chem. Intermed., 2024, 50, 2827-2840 (Scheme 39) [52].



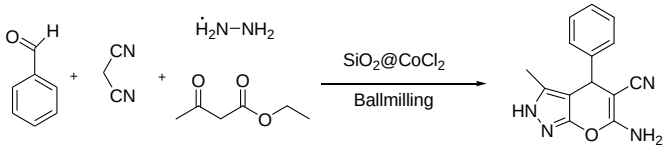
Scheme 39

Synthesis of dihydropyrano[2,3-*c*] pyrazolen derivatives in aqueous medium is carried out by Fuse et al. from aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate catalyzed by cyanuric acid and 1-methyl imidazole (Scheme 40) [53].



Scheme 40

Silica supported cobalt chloride and cobalt nitrate were investigated for the synthesis of pyranopyrazole via the four component condensation of aldehyde, malononitrile, ethylacetoacetate and hydrazine hydrate by Mobinikhaledi et al. (Scheme 41) [54].



Scheme 41

II. CONCLUSION

This review has covered the one-pot four component condensation of the s reactants to give 1,4-dhydro pyrano [2,3-*c*] pyrazole derivatives over the period of 2016 to 2025 by one-pot four components over the last ten years. Most of the methods used classical and non-classical methods for the synthesis of 1,4-dihydro pyrano [2,3-*c*]pyrazoles. In the last decade various methods are used such as microwave irradiation, sonication reflux condition use of greener solvents' and use of different catalysts such as use of ionic liquid, basic catalyst, inorganic salts, nano-catalyst, nano-composite, supported nano-materials, and use of light. In summary it is observed that new methods less hazardous, eco-friendly and uses greener solvents and minimum amount of catalysts for the preparation of 1,4-dhydro pyrano [2,3-*c*] pyrazole derivative.

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