Synthesis of Pyranopyrazoles Using An Efficient Catalyst Potassium Iodide

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Abstract- *A mixture of aldehydes , ethyl aceto-acetate ,hydrazine hydrate ,malononitrile in water was stirred at room temperature by using efficient catalyst potassium iodide in one pot to get pyranopyrazoles. This method has the advantages of simple work-up, good yields.*

Keywords- Aldehydes , ethyl aceto-acetate ,hydrazine hydrate ,malononitrile , potassium iodide,pyranopyrazole

I. INTRODUCTION

Pyranopyrazole have played a crucial role in the history of heterocyclic chemistry. It is very beneficial due to wide variety of biologically activity. Continuous efforts have been devoted to the development of general and versatile synthetic methodologies to this class of compounds.

II. LITERATURE REVIEW

Many synthetic routes of pyranopyrazole have been reported. These are single or multisteps, and two-component or multicomponent reactions (three or more compound) to get pyranopyrazole. Benefit of multicomponent reactions are more efficiency, simple, low cost, reduces waste, less reaction times.

In 1974 Otto(1) first synthesize by intiating reaction by the base-catalyzed cyclization of 4-aryliden-5-pyrazolone.
In 1981 Otto and Schmelz(2) performed with weak base which used for a Michael-type cyclization.

Klokol(3) devloped the direct conversion of 3-methyl-3-pyrazolin-5-one with malononitrile in the presence of a weak base.

III. EXPERIMENTAL

3.1. Experimental section:

All chemical were purchased from Merck, sdfcl were commercially available and were used as such.All reaction carried out at room temperature. Melting points were measured by open capillary method .

3.2. Experimental procedure for the synthesis of pyranopyrazole:

In a round bottomed flask, a mixture of one mole of malononitrile , one mole of ethyl acetoacetate , one mole of hydrazine hydrate , one mole of aldehyde ,potassium iodide with 10 ml water, stirred at room temperature for 25 mint . Reaction is monitored by TLC .The precipitate obtained was filtered off , washed with water then purified by recrystallizatin from isopropyl alcohol to get corresponding pyranopyrazole in pure form.

Reaction

3.3. Experimental table: - synthesis of pyranopyrazoles from various aldehyde

Entry	Aldehyde	Colour	Product %	Melting poitnt
1	Benzaldehyde	White ppt	95	245-259
2	4-Cl Benzaldehyde	Yellow ppt	90	235-240
3	Di- methyl amine-benzaldehyde	Red orange	86	185-195
4	Vanillin	yellow	88	210-215
5	4-Br benzaldehdye	White ppt	91	197-202
6	2-Cl benzaldehyde	Yellow ppt	85	230-238
7	4-methoxy benzladehyde	White ppt	92	200-208

3.4.Spectral data for some product: (Characterization of compounds)

Entry -2 . Yellow solid (235-240)

6-amino-3-methyl-4—(4- chlorophenyl)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
IR- 3809,3484,3346,3231,3099,3035,2228,2193,1870,1589 cm-1
H-NMR-(300MHz-DMSO) δ1.77 (s.3H) , δ 4.67(s,1H) , δ6.55(s,2H), δ7.35 , δ8.09(2H), δ11.95(s1H)
C-NMR- δ10.21,36.33 , 97.37 , 120.99,128.67,129.54,131.96,135.99,143.47,155.19,161.27

Entry 3 (red orange) (185-195)

6-amino-3-methyl-4—(dimethyl amino)-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile
IR-3441,3142,2173cm-1
NMR-(300MHz-dmso) δ 1.78(s,3H), δ 2.86(s,6H), δ 4.41(s,1H) , δ 6.01-6.62(,Ar-H), δ 6.94(dd,2H) δ 8.08-8.11(dd,2H) 11.91(s,1H)

IV. RESULTS AND DISCUSSION

When the reaction carried out in without of catalyst, reaction in not complete.. When aldehyde was treated with equimolar amount of malononitrile, ethyl aceto acetate and hydrazine hydrate in presence of catalyst potassium iodide with 10ml water vigorously stirred at room temperature for 25 mint .The precipitation obtained was filtered off . Water is very useful organic solvents. water is used as a green solvent due to low cost, easily available, not harmful, nonpolluting, and nonflammable.

V. CONCLUSION

Synthesis of pyranopyrazole has carried out by the reaction of aldehyde .malononitrile, ethyl acetoacetate and hydrazine hydrate in water using potassium iodide as catalyst. The reacton is simple workup & good yield.

VI. ACKNOWLEDGMENT

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