BAKER'S YEAST CATALYSED KNOEVENAGEL CONDENSATION OF ARYL ALDEHYDES WITH MALONONITRILE UNDER NON-AQUEOUS MEDIA

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Abstract:
Baker's yeast (BY) efficient catalyst for organic transformation. A well planned, budget Reducing, eco-friendly deals will created for the Knoevenagel condensation reaction of benzaldehyde with active methylene in nonaqueous solvent taking very cheaply, easily available biocatalyst, baker yeast. The baker yeast better results in organic solvent, methanol with no any changes in catalytic power. In this reaction malononitrile contain highly active methylene group therefore selected for this reaction. Different derivatives of benzaldehyde with active methylene group of malononitrile used for this reaction. Synthesize product will be confirmed by using spectral analysis.

Keywords: Baker's yeast, Knoevenagel, Condensation, Malononitrile

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1. Introduction

Knoevenagel reaction is best classical organic reactions of immense importance within the formation of carbon carbon bonds. A large vary of helpful merchandise are synthesized victimization the condensation. It's been produces a substituted alkenes, Cyanides, carboxylic acid, drugs and synthetic polymers.[1-3]

Knoevenagel reaction of malononitrile and aryl aldehydes is a highly demanding adduct for synthesis important organic midways and biologically precious molecules such as sugar molecule and heterocyclic compound.[4-7]

Reaction of aryl aldehydes with malononitrile is best methods for synthesis of alkene.[8] Fact that the Knoevenagel reaction is reported in 1898, many benefits like reaction simple reaction, normal conditions and some application in classical research.[9] Due to the benefits of reaction, have been design green protocol.

Knoevenagel reaction of aryl aldehyde with malononitrile in organic solvent under mild conditions. Ondruschka *et al.* Experimental analysis of known reactions by using aryl aldehyde with malononitrile in organic solvent in 30 ^{0}c. The formation of compound by reaction aryl aldehyde with malononitrile was converted to benzofurane-2-carbonitrile, mechanism via intra-molecular ring formation and remove of water.[10-15]

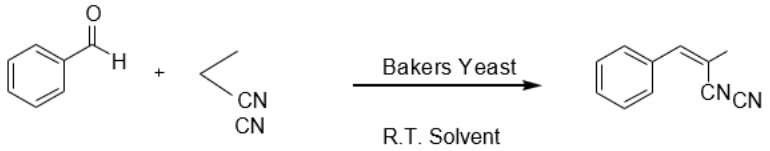
Organic reactions under organic solvent by using biocatalyst we have unexperienced output of the increasing realization of chemical changes. Biocatalytic transformation are more typical reaction with many benefits such as expand selectivity, minimize energy utilization, overcome waste, harmfulness and budget value.[16-20]

Considering the above fact, we develop an efficiency methodology, Knoevenagel reaction of aryl aldehydes with malononitrile in nonaqueous solvent in normal condition by taking simple Baker's yeast.[21-24]

1. Result and Discussion

We describe a systematic and eco-friendly Knoevenagel condensation of malononitrile and aldehydes in organic medium with mild condition by employing baker's yeast as catalyst. In arrangement of experimental setup, we taking aryl aldehyde (1a) and malononitrile by using baker's yeast as traditional standard reaction.

We observed that the effect of solvent on yield and time of reaction, standard reaction was proceed in various solvent, Starting of solvent from Ethanol (EtOH), reaction stir with 2 hrs with 68 % proceed in this solvent (**Table-1 Entry 1**) aryl aldehyde then we taking organic solvent like Methanol (MeOH), Ethyle acetate ($CH_3COOC_2H_5$) Acetone (CH_3COCH_3, Acetonitrile (ACN), Toulene ($C_6H_5CH_3$) (**Table-1 Entry 2-6**). Reaction proceed in all organic solvent except toluene, but it was interesting that resulting product are high yield in methanol, methanol has better yield of product(**3a**) and minimum time for achieve the goal of reaction (**Table 1 Entry 2**). Therefore methyl alcohol was selected for model reaction.



Benzaldehyde (1a) **Malononitrile (2)** **2-benzylidenemalononitrile (3a)**

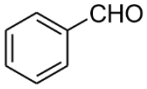
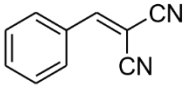
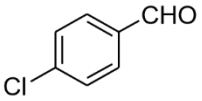
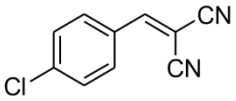
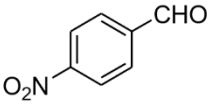
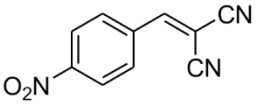
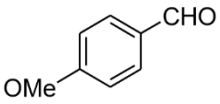
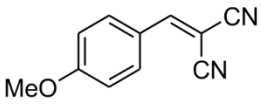
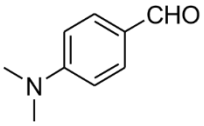
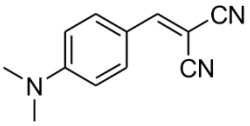
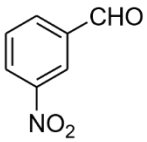
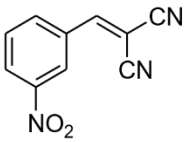
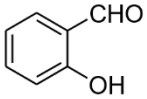
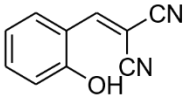
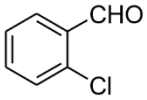
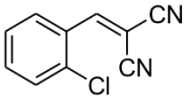
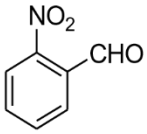
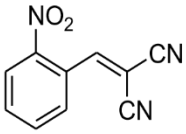
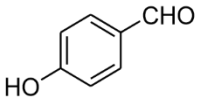
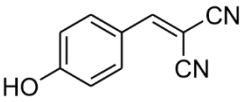
Table 1: Screening of solvent on synthesis of desired product using of benzaldehyde and malononitrile.[a]

S.N	Solvent	Time(hrs)	Yield (%)
1	Ethanol	2	68.00
2	Methanol	2	72.00
3	Ethyl Acetate	3	60.00
4	Acetone	5	50.00
5	Acetonitrile	5	40.00
6	Toluene	No Reaction	-

[a]Reaction condition (benzaldehyde 0.5 g, malononitrile 0.9 g, bakers' yeast 2 gm. and 20 ml solvent at 30 ^{0}c
[b]isolated yields

To analyse this reactions the derivatives of aryl aldehyde reacted with malononitrile **(Scheme 1)** by using baker's yeast in methyl alcohol to get final product in average yields **(Table 2, Entry 1-10).**

Table 2 : Reaction of aryl aldehyde with malononitrile by using baker's yeast.

S.N.	Note	Aromatic aldehyde	Product	Time(hrs)	Yield (%)	M.P.(^{0}c)
1	3A			2	72.00	84
2	3C			2	82.00	90
3	3C			2.5	69.00	95
4	3D			2.5	70.00	65
5	3E			2.5	70.00	70
6	3F			2.5	65.00	85
7	3G			2.5	65.00	80
8	3H			3	68.00	65
9	3I			3	77.00	75
10	3J			3	70.00	80

[a] Reaction condition (aryl benzaldehyde 0.5 g, malononitrile 0.9 g , 2 gm baker's yeast and 20 ml methyl alcohol at 30 ^{0}c
[b]-product yield

When malononitrile was added on aryl aldehyde with electron donating and withdrawing group in high percentage yield of the products **(Table 2, Entry 2-10.**

To investigate the catalytic potency of baker yeast, the reaction will proceed without baker's yeast in methyl alcohol but no any conversion after 2 hrs. From above observation, bakers' yeast is extremely important for formation carbon carbon bond by taking aryl aldehyde with malononitrile.

Bakers' yeast is biocatalyst and it contain many enzymes are present. A base is required to catalyse Knoevenagel condensation reaction and in every enzyme histidine is present which contain imidazole as basic site.[25] The histidine present, might have acting as a base in this transformation. Thus histidine accept highly acidic hydrogen of malononitrile and formation of carbanion takes place and this carbanion ion then attacks on beta carbon of unsaturated aldehyde compound. Thus there is formation of carbon carbon bond and enolate ion, finally they converted to keto form to give final products (**3A-J**)

[c] Synthesized Product are characterised by Melting point , ^{1}H NMR, ^{13}C NMR

2. Conclusion

Final conclusion that First time baker yeast is used to carried out Knoevenagel condensation of malononitrile and aldehydes in methanol. The overall synthetic process is green and high yielding.

Thus further studies on some preparation of heterocyclic compound is carried out.

4.1 General

Most of Chemicals we are used from Alfa Aesar and some chemical are used from sigmaaldrich. Baker's yeast purchase from native provider.1H NMR and 13C NMR Spectra was characterised in sophisticated analytical instrumentation facility (SAIF), University of Punjab at close tempreture in CDCl3 solvent.

4.2 Experimentation-

A mixture of aryl aldehyde (0.5 g), with malononitrile (0.9 g) was stirred at 30 ^{0}c in methyl alcohol (20 ml), once homogenous solution is created then baker's yeast (2 g) is added in R. B. Flask. Then reaction was proceed at 30 ^{0}c, the monitoring of the reaction by T.L.C. method, once a pair of hours reaction composition was filtered out to remove the catalyst and get final product. Final product was purification by using column chromatography.

Spectral characterisation of synthesize compound

2-benzylidenemalononitrile (3a): White solid, Melting point is 84 ^{0}c

^{1}H NMR (400 MHz, CDCl3) δ (ppm): 7.14 (doublet, 1H), 7.21 (double doublet, 1H) 7.30 (double doublet, 1H), 7.93(Singlet, 1H)

^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) : 69.3, 113.7, 126.41, 128.0, 128.7,135,155

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