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Bushra Saleh Samer

Organic Chemistry Research
Laboratory, School of Chemical
Sciences Swami Ramanand
Teerth Marathwada University,
Vishnupuri, Nanded-43606,
India.

V. T. Kamble

Organic Chemistry Research
Laboratory, School of Chemical
Sciences Swami Ramanand
Teerth Marathwada University,
Vishnupuri, Nanded-43606,
India.

Cesium Carbonate as Heterogeneous Catalyst For Synthesis of 3,4-Dihydro pyrano[c]chromene

Bushra Saleh Samer, VT Kamble

Abstract

An efficient and novel methodology has been developed using Caesium carbonate as efficient and recyclable base catalyst for the synthesis of 3, 4 dihydropyrano[c] chromene derivatives by one pot three component of aromatic aldehydes, malononitrile and 4-hydroxycoumarin irradiated using visible light. This method minimum the environment pollution and gives high yields of product (88-95%) in the short time (30-60 min).

Keywords: Cesium carbonate, heterogeneous, visible light, 3, 4-dihydropyrano[c] chromene

1. Introduction

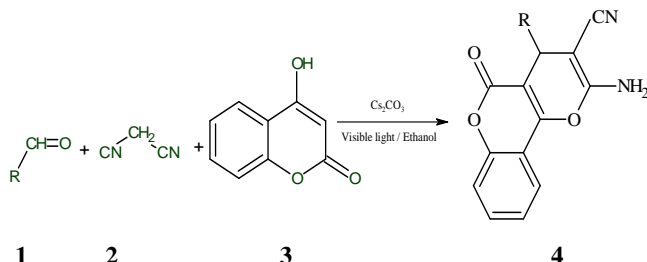
Multi-component reactions have attention attract a lot of chemists because of them are power tools for synthesis compounds having a biologically active and pharmaceutical property [1]. Multi-component reactions the suitable solution for many difficult which may face researches during synthesized process, MCRs are more efficient, less cost and less wasteful compared to classical multistep synthesis [2a-c]. In MCRs combine three compounds or more leading to a single product retains all or most of the starting molecules [3]. MCRs have been successful in the synthesis of 3, 4 dihydropyrano [c] chromenes and their derivatives which considerable interest due to they have pharmaceutical and biological properties [4], like spasmolytic [5], anti-inflammatory [6], anticancer [7], molluscicidal [8], diuretic [9], anti-coagulant [10]. A wide variety of methods and catalysts employed for synthesis of 3,4 dihydropyrano [c] chromenes such as TBAB [11], K₂CO₃ [12], pyridine [13], Ammonium acetate [14], MgO [15], diammonium hydrogen phosphate [16], polymer supported sulphanilic acid [17], SiO₂PrSO₃H [18], basic ionic liquid [19], CuO nanoparticles [20], p-dodecylbenzenesulfonic acid [21], trisodiumcitrate [22] TiO₂ [23], Amberlyst A21 [24] and 4-(dimethylamino) pyridine (DMAP) [25]. Although that pervious methods [11-25] have own its merits but it's suffer from disadvantages such as harsh reactions conditions, tedious procedure, utilize toxic reagents and solvents and poor yields of products. For these reasons the search about methods are more efficient, less consume of reagents and catalyst in short time, more friendly of environment and to give excellent yields of product are demand. In the last years concentrated many of researches of the catalysis by heterogeneous materials as they have many of advantages and applications which confer distinction upon others homogenous catalysts such as insolubility in the water and organic solvents, recovered them from media of reaction easily as compared to homogenous catalysts which soluble in reaction solvents so recovered process from reaction media become somewhat difficult, an addition to cheap of heterogeneous catalysts and its thermal stability in contrast to homogeneous catalysts which characterized being expensive and thermal instability, in the same time homogenous catalysts have feature over heterogeneous catalysts such as its more selectivity and possess many of active sits [26-28]. Herein our work select cesium carbonate as heterogeneous catalyst and solid base which describe being cheap, nontoxic and can recoverable and reusable many runs without loss its activity.

Cesium carbonate used in many of reactions such utilized as in knovengeal reaction [29] synthesis of 2-amino thiophenes with Gewald reaction [30] and it is also used for N-alkylation of amines [31]. For our knowledgement this first time use cesium carbonate as catalyst for synthesis 3,4-dihydropyrano[c]chromene (4) in assisted visible light irradiation by condensation three components of aromatic aldehydes (1), malononitrile (2), and 4-hydroxycoumarin (3) as shown in the scheme (1)

Correspondence:

Bushra Saleh Samer

Organic Chemistry Research
Laboratory, School of Chemical
Sciences Swami Ramanand
Teerth Marathwada University,
Vishnupuri, Nanded-43606,
India.



Scheme 1: Photochemical synthesis of 3,4 dihydropyrano[c]chromene

2. Experimental

2.1 Materials and methods

Melting points were recorded in open capillary and were uncorrected. The progress of the reaction was monitored by thin layer chromatography (TLC) which performed in the presence petroleum ether and ethyl acetate (8:2) on silica plates. Infrared (IR) spectra were recorded on a Bruker equinox-55 spectrometer using KBr discs, ^1H NMR spectra were recorded at 400 MHz using DMSO as solvent with TMS as an internal standard.

2.2 General procedure for the synthesis derivatives of 3, 4 dihydropyrano[c]chromene

A mixture of aldehyde (1mmol), malononitrile (1mmol), 4-hydroxycoumarin (1mmol) and cesium carbonate (10mol%) dissolved in 5 ml of ethanol and irradiated with 200W tungsten lamp for appropriate time. upon on the complete the reaction (monitor by thin-layer chromatography TLC, the reaction mixture allowed to cooled to room temperature and poured into on ice water which filter to separate the product from the catalyst, wash the product 2-3 times by water then dry it in the room temperature and recrystallization from hot ethanol to afford the corresponding 3,4-dihydropyrano[c]chromene, for recovered the cesium carbonate the aqueous layer was evaporated under reduced pressure to yield the catalyst which can reuse many times, all the products are characterized by IR and $^1\text{HNMR}$ and comparison the results with authentic samples.

2.3 Spectral data for some the compounds

2-Amino-4-phenyl-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile

White solid, mp = 254-256 °C, IR (KBr) ν_{max} 3383, 3280, 3172, 2196, 1709, 1670, 1605, $^1\text{HNMR}$ (DMSO- d_6 , 400MHz), μ = 4.45(s, 1H), 7.25(d, 2H, J=7.8Hz), 7.28(s, 1H), 7.33(t, 1H, J=7.5Hz), 7.42(s, 2H), 7.56(t, 1H, J=7.6Hz), 7.65(t, 1H, J=7.5Hz), 7.92(d, 1H, J=7.8Hz)

2-Amino-4-(4-nitrophenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile

Yellow solid, mp = 258-260°C, IR (KBr) ν_{max} 3481, 3367, 2194, 1714, 1668, 1605.

$^1\text{HNMR}$ (DMSO- d_6 , 400 MHz), μ = 4.65 (s, 1H), 7.47(d, 1H, J=8.4Hz), 7.55(t, 1H, J=7.8Hz), 7.57(s, 2H), 7.65(d, 2H, J=8.0Hz), 7.69(t, 1H, J=7.8Hz), 7.91(d, 1H, J=7.8Hz).

2-Amino-4-(4-chloro phenyl)-4, 5 dihydro-5-oxopyrano [3,2-c] chromene-3-carbonitrile

White solid, mp = 250-252°C, IR (KBr) ν_{max} 3375, 3288, 3186, 2194, 1708, 1675, 1605, $^1\text{HNMR}$ (DMSO- d_6 , 400MHz), μ = 4.47(s, 1H), 7.32(d, 2H, J=8.2Hz), 7.36(s, 2H), 7.38(s, 2H), 7.44(d, 1H, J=8.2Hz), 7.63(t, 1H, J=7.6Hz), 7.68(t, 1H, J=7.8Hz), 7.92(d, 1H, J=7.8Hz).

2-Amino-4-(4-hydroxyphenyl)-4,5-dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile

White solid, mp = 262-264°C, IR(KBr) ν_{max} = 3390, 2360, 2339, 2193, 1703, 1669, 1608, $^1\text{HNMR}$ (DMSO- d_6 , 400 MHz), μ = 4.40(s, 1H), 6.73(d, 2H, J=8.5Hz), 6.84(d, 2H, J=8.9Hz), 7.37(s, 2H), 7.40-7.72(m, 2H), 7.66(t, 1H, J=7.8Hz), 7.89(dd, 1H, J=7.7, J_2 =1.4), 8.14(s, 1H).

3. Result and discussion

Herein, the photochemical synthesis of 3,4-Dihydro pyrano[c]chromene **4** by three- component condensation of substituted aldehydes **1**, malononitrile **2**, and 4 hydroxycoumarin **3** in the presence of cesium carbonate as heterogeneous catalyst irradiated by visible light (scheme 1). to investigate the optimize conditions for synthesis 3,4-dihydropyrano[c]chromene, We selected the model of 3-nitrobenzaldehyde (1mmol), malononitrile (1mmol) and 4-hydroxycoumarin(1mmol) with respect of rate of reactions and yields of product. Firstly we examined the ideal amount of Cs_2CO_3 in synthesis of 3, 4-Dihydro pyrano[c]chromene. From results showed in the (table 1) that 95% yields of product was obtain it with 10% of cesium carbonate in the presence of ethanol as solvent (table 1, entry 3) where in the case absence of the catalyst the reaction was completed through a long time and poor yield of product (entry 1). The increasing amount of the catalyst up to 10% do not leading to improve the yield of product or decrease the time required for complete the reaction (entries 4 and 5). We next evaluated the role which play the solvents in the synthesis of 3, 4 dihydropyrano[c]chromene, among various solvent such as methanol, ethanol, water, acetonitrile and acetone the best result was obtained after 30 min using ethanol as solvent in excellent yield 95% (table 2, entry 2). In order to show applied our method in the synthesis of 3, 4 dihydropyrano[c]chromene, the reaction extended to others substituted aldehydes carrier either electrons withdrawing groups or electrons donating groups, the results presented in the table 3 showed that all aldehydes successful in this reaction. The next step was study the role which play visible light in the synthesis of 3, 4 dihydropyrano[c]chromene, when our reaction carried in room temperature and applied same reactants, 4-nitrobenzaldehyde, malononitrile and 4-hydroxycoumarin using cesium carbonate as catalyst and ethanol as solvent, the We noticed that after 10 hours of time the reaction completed and only 30% of yield was obtained while in the case use the visible light as assistant factor in excitation the reaction during short time 30 min and 95% yield of product, this indicate to significance the role which play visible light in synthesis of 3, 4 dihydropyrano[c]chromene. To show the advantages of the present work in comparison with resulted which reported in the other literature, we had compared the reaction 4-nitrobenzaldehyde, malononitrile and 4-hydroxycoumarin employed cesium carbonate as catalyst with another catalyst which carried out in different conditions such as TBAB^[11], aqueous media^[16], polymer supported sulphanilic acid^[17], TiO_2 ^[23] and DMAP^[25] all the results presented in the table 4 which showed that cesium carbonate was the best catalyst for synthesis of 3,4 dihydropyrano[c]chromene with respect to condition of reactions, time of reaction and yields of product. Finally, we investigated the possibilities of recycling the catalyst Cs_2CO_3 for the our model reaction, after the separation of product from catalyst by filtration, the catalyst washed with hot ethanol then dried under reduced vacuum which store in dried tubes for further reuse in another consecutive reaction time, our catalyst was

recycling five times without loss its activity exception loss its weight. All the results summarized in the table 5.

Table-1: Study the amount of the catalyst on synthesis 2-Amino-4-(4-nitrophenyl)-4,5 dihydro-5-oxopyrano [3, 2-c] chromene-3-carbonitrile

Entry	Amount of Cs ₂ CO ₃ mol%	Yield (%) ^b
1	no catalyst	7
2	5	45
3	10	95
4	20	95
5	30	93

^a Condition of reaction: 4-nitrobenzaldehyde(1mmol), malononitrile (1mmol)

4-hydroxycumarine (1mmol), Time: 30 min and solvent: ethanol (5ml),

^b Yield of product

Table 2: Effect of various solvents on synthesis 4b

Entry	Solvent (5ml)	Time(min)	Yield (%) ^a
1	Methanol	55	80
2	Ethanol	30	95
3	Water	180	25
4	Acetonitrile	90	77
5	Acetone	230	49

^a Isolated yield

Table 3: Synthesis of 3, 4-dihydropyrano[c] chromene by aromatic aldehyde (1mmol), malononitrile (1mmol), 4-hydroxycumarine (1mmol) and 10 mol% Cs₂CO₃

Entry	Aldehyde	Product	Time (min)	Yield (%)	M.P ^o C
1	C ₆ H ₅	4a	35	90	254-256
2	4-NO ₂ C ₆ H ₄	4b	30	95	258-260
3	4-Cl C ₆ H ₄	4c	40	93	250-252
4	3-NO ₂ C ₆ H ₄	4d	50	92	262-264
5	4-CNC ₆ H ₄	4e	35	94	280-282
6	4OHC ₆ H ₄	4f	30	88	226-228
7	4CH ₃ C ₆ H ₄	4g	60	90	251-253
8	4-CH ₃ OC ₆ H ₄	4h	35	94	268-270
9	3,4(CH ₃ O) ₂ C ₆ H ₃	4i	30	90	230-232
10	4,5(CH ₃ O) ₂ C ₆ H ₃	4j	55	93	253-255
11	4-NMe ₂ C ₆ H ₄	4k	45	85	225-227
12	4-FC ₆ H ₄	4l	35	95	260-262
13	4-BrC ₆ H ₄	4m	60	87	250-252

Table 4: Comparison of Various Catalysts for Synthesis 3,4-dihydropyrano[c]chromene by Reaction of 4-Nitrobenzaldehyde (1mmol) malononitrile(1mmol) and 4-hydroxycumarine (1mmol) using Cs₂CO₃as catalyst

Entry	Catalyst	Condition of reaction	Time(min)	Yield (%)	Ref
1	TBAB	Neat	45	86	[11]
2	(S)Proline	Reflux	120	82	[16]
3	Sulpharic acid	Reflux	90	84	[17]
4	TiO ₂	Reflux	45	90	[23]
5	DMAP	Reflux	90	82	[25]
6	Cs ₂ CO ₃	Visible light	30	95	Our work

Table-5: Evaluation reusability of Cs₂CO₃ for synthesis 2-Amino-4-(4-nitrophenyl)- 4,5 dihydro-5-oxopyrano[3,2-c]chromene-3-carbonitrile

Entry	Time of cycle	Yield %
1	1st	95
2	2nd	94
3	3rd	93
4	4th	90
5	5th	89

4. Conclusion

In conclusion, many of 3, 4 dihydropyrano[c] chromene derivatives were synthesized by an efficient, convenient, inexpensive and friendly environment method which depends on the visible light in the irradiation three reaction components of aromatic aldehyde, malononitrile and 4-hydroxycumarine catalyzed by cesium carbonate. The our procedure offer many advantages such as high yields of product, short reaction time, inexpensive and non toxic catalyst .we wish that our method has application in the synthesis of of 3, 4 dihydropyrano[c] chromene and its derivatives

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