

SCOLECITE: AS AN EFFICIENT AND REUSABLE CATALYST FOR THE SYNTHESIS OF 2-AMINO-4H-CHROMENES

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ABSTRACT

Objective: Scolecite is naturally occurring zeolite, Which contain alumina and silica in the structure. Herein we report, scolecite as an efficient and reusable catalyst for the synthesis of 2-amino-4H-chromenes from three component condensation of aromatic aldehydes, malononitrile and alpha or beta naphthol in ethanol.

Materials and Method: Solvents used were of analytical and laboratory grade. The product were prepared by reflux method and analyzed by melting points, TLC, 1H-NMR, IR and Mass spectroscopy.

Results: 2-amino-4H-chromenes synthesized successfully using scolecite as catalyst. The lewis acidic and basic sites of the scolecite enhance the rate of reaction. The electron donating and electron withdrawing group gives similar yield of products.

Conclusion: This methods offers simple, clean, fast, efficient and reusability of catalyst for the synthesis of 2-amino-4H-chromenes. Which overall contribute to the green chemistry.

Keywords: Natural zeolite, Scolecite, 2-amino-4H-chromene,

INTRODUCTION

Recently, heterogeneous solid catalysts have been used in various organic transformations as they possess a number of advantages [1-4]. Heterogeneous catalyst offers clean technology for the organic synthesis. There was green approach by using heterogeneous catalyst such as easy handling, efficient, no loss of chemical, reusability of catalyst.

Multicomponent coupling reaction (MCR) is a powerful synthetic tool for the synthesis of biologically active compounds [5-7]. Development of such multicomponent coupling reaction strategies in aqueous medium has been of considerable interest, as they provide simple and rapid access to a large number of organic molecules through a sustainable path [8].

Chromene derivatives are an important class of heterocyclic compounds having significant biological activities [9]. During the last decade, these compounds have shown interesting pharmacological properties, including antimicrobial, antiviral, antioxidant, antitumor, cancer therapy, and central nervous system activities [10-11]. Many chromenes are also photoactive and can be used in various photoinduced reactions affording diverse heterocyclic compounds [12].

2-Amino-4H-chromenes are generally prepared by refluxing malononitrile, an aldehyde and an activated phenol in the presence of hazardous organic bases like piperidine in organic solvents such as ethanol and acetonitrile for several hours [13]. Recently, relatively benign catalysts such as cetyltrimethylammonium chloride (CTACl) [14], montmorillonite KSF clay, KF/Al₂O₃ [15], TiCl₄ [16], triethylamine [17], basic alumina [18], MgO [19], Heteropolyacid [20], basic ionic liquids [21], and iodine/K₂CO₃ [22] have been used in this reaction.

However, the application of some of these methods is limited due to their moderate yields of the products, longer reaction times and laborious workup procedures.

As part of our program aimed at developing new selective and environmentally friendly methodologies for the preparation of fine

chemicals, herein we report the synthesis of 2-amino-4H-chromenes using scolecite in good to better yields.

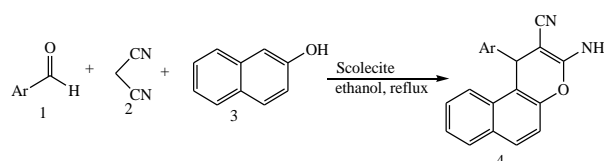
EXPERIMENTAL

MATERIALS AND METHODS

Solvents used were of analytical and laboratory grade. All melting points were taken in open capillaries in paraffin bath and are uncorrected. Thin-layer chromatography (TLC, on aluminium plates pre-coated with silica gel, 60F254, 0.25mm thickness) (Merck, Darmstadt, Germany) was used for monitoring the progress of all reactions, purity and homogeneity of the synthesized products; eluent-n-hexane:ethyl acetate (6:4). UV radiations were used as visualizing agents. IR spectra were recorded in KBr pellet on a Perkin-Elmer Spectrum GX FT-IR Spectrophotometer and only characteristic peaks were reported in cm⁻¹. ¹H-NMR spectra were recorded in DMSO-d₆ on a Bruker Advance 400 (MHz) Spectrometer. Chemical shifts were reported in parts per million (ppm).

General Procedure for the Synthesis of 2-Amino-4H-chromene Derivatives

To the mixture of the aromatic aldehyde (1 mmol), malononitrile (1 mmol), and β-naphthol (1 mmol) was added Scolecite (0.1 g) in ethanol medium. The resulting mixture was refluxed for the appropriate time (Table 2). After completion of the reaction (as indicated by TLC), the mixture was diluted with ethanol (10 mL) and the catalyst was separated by filtration. Evaporation of solvent under reduced pressure gave the product 4. Further purification was achieved by recrystallization from EtOH/H₂O.



RESULTS AND DISCUSSION

In our preliminary experiments to optimize the reaction conditions, a model reaction between benzaldehyde (1 mmol), malononitrile (1 mmol) and β -naphthol (1 mmol) was refluxed in the presence of various amounts of scolecite in ethanol medium and the results are illustrated in Table 1. The reaction also carried out without catalyst to test the catalytic efficiency and it was found that the product was 34%. The catalyst tested as 0.05, 0.1 and 0.15 g, and results presented in Table 1. From the table we conclude that 0.1 g catalyst efficient for the better yield of the product.

By keeping above catalyst amount constant, we carried out many reactions by changing the aromatic aldehyde each time and we get much better yield. The yield of the product does not affected by electron donating and electron withdrawing groups. The products

are analyzed by NMR, FT-IR and Mass spectrometer and matched with authentic data. The results are mentioned in Table 2. The recovered catalyst are again used for the same model reaction and yield were measured and it shows that the yield of products are almost same i.e. 94, 93,93%. It means that catalyst can be used without much loss in its activity.

Table 1: Screening conditions for the model reaction.

Sr. No.	Catalyst amount (g)	Time (hr)	Yield (%) ^a
1	No catalyst	4	34
2	0.05	3	52
3	0.1	1.5	94
4	0.15	1.5	94

a-yield refers to pure product.

Table2: Synthesis of 2-amino-4H-chromene derivatives.

Entry	Ar	Product	Time (hr)	Yield (%) ^{a,b}	M.P. (°C)
1	Ph	4a	1.5	94	273-274
2	3-MeC ₆ H ₄	4b	2.5	89	230-232
3	4-MeC ₆ H ₄	4c	2.0	90	260-263
4	4-OHC ₆ H ₄	4d	2.0	93	270-272
5	2-ClC ₆ H ₄	4e	1.5	87	231-215
6	4-ClC ₆ H ₄	4f	2.0	92	205-206
7	2-NO ₂ C ₆ H ₄	4g	3.0	90	238-240
8	3-NO ₂ C ₆ H ₄	4h	2.5	89	232-235
9	4-NO ₂ C ₆ H ₄	4i	2.0	94	236-239
10	4-OMeC ₆ H ₄	4j	1.5	94	185-187

a- Yields refer to pure product. b- all compound are known and spectroscopic data compared with authentic sample

CONCLUSION

In summary, we have developed an efficient method for the synthesis of 2-amino-4H-chromene derivatives by means of a three-component reaction between aromatic aldehyde, β -naphthol and malononitrile using a catalytic amount of scolecite in ethanol medium under reflux conditions. This method has several advantages including high yields of products, easy experimental workup. The reactivated catalyst reused four consecutive cycles without any significant loss in catalytic activity.

REFERENCES

- TamaddonF, FarahiM, KaramiB, J. Mol. Catal. A: Chem. 2012;356: 85.
- TamaddonF, FarahiM, Synlett2012; 1379.
- GenelotM, DufaudV, DjakovitchL, Tetrahedron 2011;67: 976.
- PhanNTS, NguyenTT, LuoQH, NguyenLTL, J. Mol. Catal. A: Chem. 2012;363: 178.
- SrivastavaRG, VenkataramaniPS, Synthetic Communications, 1988; 18: 1537.
- ShenM, DriverTG, Organic Letters, 2008; 10: 3367.
- BahramiK, KhodaciMM, NaaliF, Journal of Organic Chemistry, 2008; 73: 6835.
- VarmaRS, Green Chemistry, 1999; 1: 43.
- DongZ, LiuX, J. Feng, M. Wang, L. Lin, X. Feng, Eur. J.Org. Chem. 2011; 137.
- YuH, GuoH, LiX, J. Heterocycl. Chem. 2011;48: 1264.
- IaroshenkoVO, MkrtchyanS, GevorgyanA, MiliutinaM, VillingerA, VolochnyukD, SonovskikhVY, LangeP, Org. Biomol. Chem. 2012;10: 890.
- KrayushkinMM, LevchenkoSK, YarovenkoNV, ZavarzinIV, BarachevskyVA, PuankovYA, ValovaTM, KobelevaOI, ARKIVOK 2009;ix: 269.
- Elagamay AGA, El-Taweel FMAA, Indian J. Chem. B 1990;29: 885.
- Ballini R, Bosica G, Conforti ML, Maggi R, Mazzacanni A, Righi P, Sartori G, Tetrahedron 2001;57: 1395.
- Ballini R, Bigi F, Conforti ML, Catal. Today 2000;60: 305.
- Wang, X, Shi D, Tu S, Synth. Commun. 2004;34: 509.
- Kumar BS, Srinivasulu N, Dupuri RH, Russ. J. Org. Chem. 2006;42: 1813.
- Maggi R, Ballini R, Sartori G, Tetrahedron Lett. 2004;45: 2297.
- Kumar D, Reddy VB, Mishra BG, Tetrahedron 2007;63: 3093.
- Heravi MM, BakhtiariKh, Zadsirjan V, Bamoharramb FF, Heravi OM, Bioorg. Med. Chem. Lett. 2007; 17: 4262.
- Gong, K, Wang, HL, Fang, D, LiuZL, Catalysis Communications 2008;9: 650.
- Ren, YM, Cai, Ch. Catalysis Communications 2008; 9: 1017.