International Journal for Pharmaceutical Research Scholars (IJPRS)

V-4, I-3, 2015 ISSN No: 2277 - 7873

RESEARCH ARTICLE

Knoevenagel Condensation by Employing Natural Catalyst- A Green Chemistry Approach

Pravin Chavan*[1], Pravinkumar Nagore[1], Kanchan Mane[1], Sachin Bangale[2]

[1]*Department of Chemistry, M.T.E.S. Doshi Vakil Arts & G.C.U.B. Science & Commerce College, Goregaon-Raigad (M.S.) India.*

[2]*Department of Chemistry, Shri. Gopinath Mahadev Vedak College of Science, Tala-Raigad 402111(M.S.) India.*

Manuscript No: IJPRS/V4/I3/00144, Received On: 13/07/2015, Accepted On: 23/07/2015

ABSTRACT

A simple, green method for condensation of substituted aromatic aldehydes with malanonitrile catalyzed by extract of henna leaves at room temperature in absence of any chemical reagents. The products were purified by recrystallisation method and were identified along with their by spectroscopic methods: NMR and IR spectroscopy.

KEYWORDS

Henna Leaves, Natural Catalysis, Aldehyde, Malononitrile

INTRODUCTION

The Knoevenagel condensation[1] is mostly useful for the formation of carbon-carbon bonds[2-3]. Generally, Knoevenagel condensation is catalyzed by using bases such as amines and their ammonium salts, etc. as well as weak acids such as Lewis acids- $ZnCl_2$[4], LiCl[5], $TiCl_4$[6], Al_2O_3[7] etc.

However, the use of such acids bases and solvents in large scale has led to many ecological problems i.e. the necessity to dispose organic waste due to the formation undesirable side products resulting from polymerization and self-condensation along with the total dissolve salt form during the neutralization of the catalysts. As a result, cation exchanged zeolite[8], modified inorganic solids[9], ion exchange resin[10], Schiff supported MCM-41[11-12] have been introduced as new catalysts.

***Address for Correspondence:**
Sachin Bangale
Department of Chemistry,
Shri. Gopinath Mahadev Vedak College of Science,
Tala-Raigad 402111(M.S.)
India.
E-Mail Id: bangale_sv@rediffmail.com

A number of organic reactions using natural catalysts such as clay[13-14], natural phosphates[15-17], animal bone[18] and various fruit juices are reported due to acidic nature aqueous fruit juice like lemon[19-27], pine apple[28-29], coconut[30], tamarinds indica[31] etc.

The present work concerns about environmental demands and development of eco-friendly, non hazardous method for the formation of carbon-carbon bond using inexpensive henna leaves extract as a natural catalyst with excellent yield. Henna leaves contains Lawson, Gallic acid, Tannin, Sugars etc. The reaction was carried out at RT with constant stirring by taking equimolar quantities of aromatic aldehydes and malanonitrile in presence of stoichiometric amount of henna extract without any organic solvents to give methylene malononitrile.

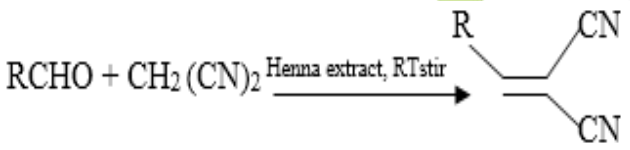
EXPERIMENTAL

Henna leaves were collected from nearby forest as shown in Figure No.1. Leaves were cleaned under running water and extract prepared using mortal and pastel. Extract was filtered using filter

paper and juice was used to carry out Knoevenagel condensation.

Figure 1: Henna leaves

Scheme-1



Instruments

IR spectroscopy was carried out using Spectrum BX instrument model L1050033.

General Method for the Condensation of Aldehydes with Malononitrile

Different aromatic aldehydes (10mmol), Malononitrile (10mmol) and henna juice (1ml, pH = 4.5 to 5.3) were taken in a round bottom flask and stirred using magnetic stirrer. The reaction time varied from 30 to 90 min monitored by TLC. Upon completion of the reaction, the reaction mixture was taken into watch glass and purified by recrystallization method using alcohol as a solvent. Identity of compounds confirmed by ^{1}H NMR spectra, IR spectra and M.P.

RESULTS AND DISCUSSION

In the present research paper we have reported an efficient eco-friendly and economic catalyst for Knoevenagel condensation of aromatic aldehydes with active methylene group to give substituted methylene malononitrile.

In addition to easy way, this catalyst resulted in higher yields for the synthesis products (Tab-1), in the knoevenagel condensation. Furthermore the work up is simple and user friendly.

Spectral Data

2-(Phenylmethylene) malononitrile **(a):** Light yellow crystal, yield: 88 %, mp 83ºC (82-83ºC). FTIR (KBr, ν_{max} (cm^{-1})) 2223 (CN), 1598 (C=C). ^{1}HNMR (300 MHz, CDCl, 25ºC): d = 7.9 (d, *J*=8.5 Hz, 2 H, phenyl), 7.8 (s, 1 H, CH), 7.5–7.7 (m, 3 H, phenyl) ppm.

2-[(4-Chlorophenyl) methylene] malononitrile **(b):** Colorless crystals, yield: 93%, mp 165ºC (163-165ºC). FTIR (KBr, ν_{max} (cm^{-1})) 2223 (CN), 1582 (C=C). ^{1}HNMR (300 MHz, CDCl3Hz, 2H, phenyl) ppm. , 25ºC): d = 7.8 (d, *J*= 8.4 Hz, 2H, phenyl), 7.7 (s, 1H, CH), 7.5 (d, *J*= 8.4 Hz, 2H, phenyl) ppm.

2-[(4-Methoxyphenyl) methylene] malononitrile **(c):** Pale yellow crystals, yield: 85%, mp 112-114ºC (114-115ºC), FTIR (KBr, ν_{max} (cm^{-1})) 2218 (CN), 1598 (C=C). ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): d = 7.9 (d, *J*=8.5 Hz, 2H, phenyl), 7.6 (s, 1H, CH), 7.0 (d, *J*=8.5 Hz, 2H, phenyl), 3.9 (s, 3H, OCH_3) ppm.

2-[(3-Nitrophenyl) methylene] malononitrile **(d):** Off-white crystals, yield: 92, mp 104ºC (104-105ºC) FTIR (KBr, ν_{max} (cm^{-1})) 2228 (CN), 1592 (C=C), 1521 (NO_2, asymmetric), 1349 (NO_2, symmetric). ^{1}HNMR (300 MHz, $CDCl_3$, 25ºC): d = 8.4 (s, 1H, phenyl), 8.2 (s, 1H, CH), 7.4-8.1 (m, 3H, phenyl) ppm.

2-[(4-Nitrophenyl) methylene] malononitrile **(e):** Pale yellow crystal, yield: 88%, mp 163ºC (160-162ºC) FTIR (KBr, ν_{max} (cm^{-1})) 2226 (CN), 1592 (C=C), 1523(NO_2, asymmetric), 1349 (NO_2, symmetric). ^{1}HNMR (300 MHz, $CDCl_3$, 25ºC): d = 8.2–8.0(d, *J*=10.0 Hz, 2H, phenyl), 7.8 (s, 1H, CH), 7.7–7.6 (d, *J*=10.0 Hz, 2H, phenyl) ppm.

Mechanism

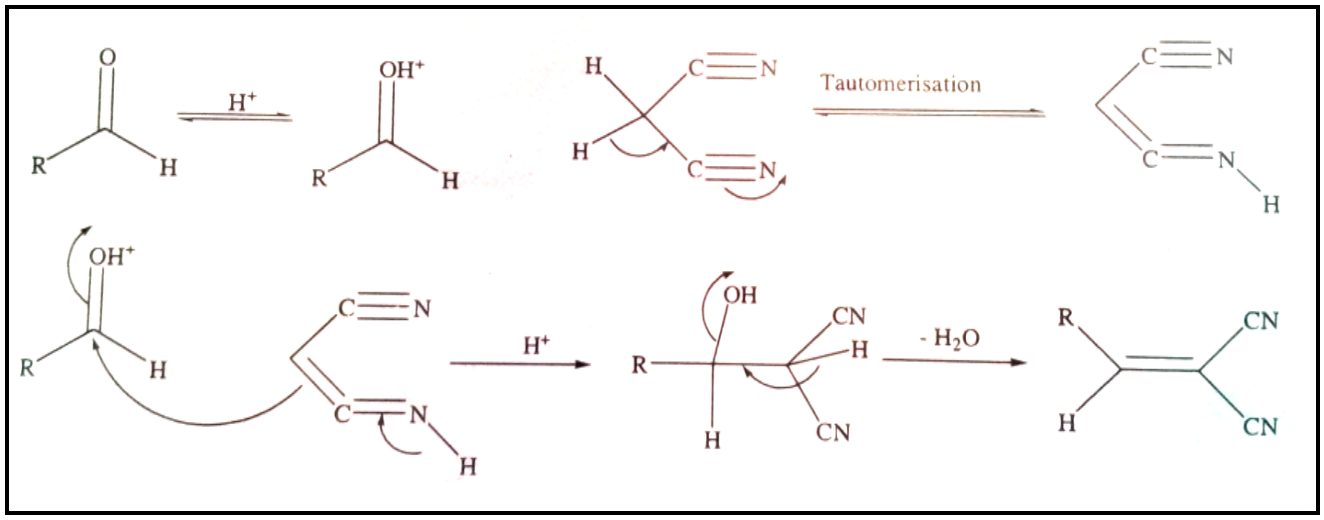
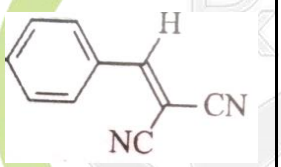
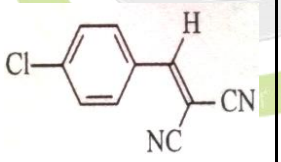
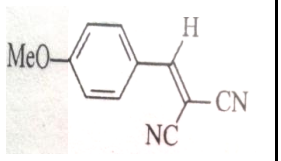
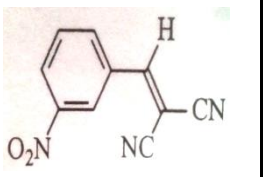
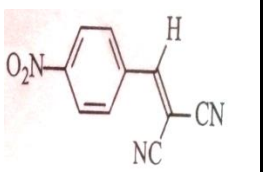


Table 1: Results of Knovenagel condensation of malononitrile with aldehydes catalyzed by Henna leaves (extract)

	Substrate	Product	Color and nature of product	Yield (%)	Time (min)	M.P. (ºC)
a.	Benzaldehyde		Light yellow crystals	88	32	83
b.	4-Chlorobenzaldehyde		Colorless crystals	90	40	164
c.	4- Methoxybenzaldehyde		Yellow crystals	86	25	116
d.	3-Nitrobenzaldehyde		Off-white crystals	90	30	104
e.	4-Nitrobenzaldehyde		Pale yellow crystals	94	38	163

CONCLUSION

An eco-friendly and economic method has been developed to carry out the Knoevenagel condensation by henna juice catalyst with good yields. This solvent free approach is based on green chemistry principles and do not cause any harm to environment. In addition, it involves mild reaction condition and simple work up.

ACKNOWLEDGEMENT

Authors are thankful to Honorable Principal Dr. G. D. Giri, B. T. Vibhute and N. G. Vedak for providing necessary facilities during the research work.

REFERENCES

1. Knoevenagel, E. (1894). Ueber eine darstellungsweise der glutarsäure. *Berichte Der Deutschen Chemischen Gesellschaft*, *27*(2), 2345-2346.
2. Knoevenagel, E. (1898). Condensationen zwischen malonester und aldehyden unter dem einfluss von ammoniak und organischen aminen. *Berichte Der Deutschen Chemischen Gesellschaft*, *31*(3), 2585-2595.
3. Tietze, L. F., Beifuss, U., Trost, B. M., & Fleming, I. (1991). Comprehensive organic synthesis. *Trost, BM, Fleming, I.* Pergamon Press: *Oxford, UK*, 341-394.
4. Rao P. S. & Venkataratnam R. V. (1991). *Tetrahedron Letters*, 32, 5821.
5. Sabhitha G., Reddy B. V. Babu R. S. & Yadav J. S., 1998. *Chemistry Letters*, 27(8), 773.
6. Lehnert W. (1970). *Tetrahedran Letters*, 54, 4723.
7. Texier-Boullet F. & Foucaud A. (1982). *Tetrahedron Letters*, 23, 4927.
8. Reddy T. I. & Varma R. S. (1997), *Tetrahedron Letters*, 38, 1721.
9. Abdallah-EI Ayoubi S. & Texier-Boullet F. (1995). *Journal of Chemical Research (S)*, 205.
10. Angeletti E., Canepa C., Martinetti G., & Venturello P. (1989). *Journal of Chemical Society, Perkin Trans 1*, 105.
11. Simpson J., Rathbone D. L. & Billington D. C. (1999). *Tetrahedron Letters, 40*, 7031.
12. Dog X., Hui Y., Xie S., Zhang P., Zhou G. & Xie Z. (2013). RSC *Advances, 3*, 3222.
13. Ramesh, E., & Raghunathan, R. (2009). Microwave-Assisted K-10 Montmorillonite Clay–Mediated Knoevenagel Hetero-Diels–Alder Reactions: A Novel Protocol for the Synthesis of Polycyclic Pyrano [2, 3, 4-kl] xanthene Derivatives. *Synthetic Communications®*, *39*(4), 613-625.
14. Habibi, D., & Marvi, O. (2006). Montmorillonite KSF and Montmorillonite K-10 clays as efficient catalysts for the solventless synthesis of bismaleimides and bisphthalimides using microwave irradiation. *Arkivoc*, *13*, 8-15.
15. Chakrabarty, M., Mukherji, A., Arima, S., Harigaya, Y., & Pilet, G. (2009). Expeditious reaction of ninhydrin with active methylene compounds on montmorillonite K10 clay. *Monatshefte für Chemie-Chemical Monthly*, *140*(2), 189-197.
16. Wada, S., & Suzuki, H. (2003). Calcite and fluorite as catalyst for the Knoevenagel condensation of malononitrile and methyl cyanoacetate under solvent-free conditions. *Tetrahedron Letters*, *44*(2), 399-401.
17. Zahouily, M., Mounir, B., Charki, H., Mezdar, A., Bahlaouan, B., & Ouammou, M. (2006). Investigation of the basis catalytic activity of natural phosphates in the Michael condensation. *Arkivoc*, *13*, 178-186.
18. Zahouily, M., Bahlaouan, B., Rayadh, A., & Sebti, S. (2004). Natural phosphate and potassium fluoride doped natural phosphate: efficient catalysts for the construction of a carbon–nitrogen bond. *Tetrahedron Letters*, *45*(21), 4135-4138.
19. Sebti, S., Smahi, A., & Solhy, A. (2002). Natural phosphate doped with potassium fluoride and modified with sodium nitrate:

Efficient catalysts for the Knoevenagel condensation. *Tetrahedron Letters*, *43*(10), 1813-1815.

20. Riadi, Y., Mamouni, R., Azzalou, R., Boulahjar, R., Abrouki, Y., El Haddad, M., & Lazar, S. (2010). Animal bone meal as an efficient catalyst for crossed-aldol condensation. *Tetrahedron Letters*, *51*(51), 6715-6717.
21. Deshmukh, M. B., Patil, S. S., Jadhav, S. D., & Pawar, P. B. (2012). Green approach for Knoevenagel condensation of aromatic aldehydes with active methylene group. *Synthetic Communications*, *42*(8), 1177-1183.
22. Patil, S., Jadhav, S. D., & Deshmuk, M. B. (2011). Natural acid catalyzed multi-component reaction as a green approach. *Archives Applied Science Research*, *3*(1), 203-208.
23. Sachdeva, H., Saroj, R., Khaturia, S., & Dwivedi, D. (2013). Environ-economic synthesis and characterization of some new 1, 2, 4-triazole derivatives as organic fluorescent materials and potent fungicidal agents. *Organic Chemistry International*, *2013*.
24. Patil, S., Jhadav, S. D., & Patil, U. P. (2012). Natural acid cata-lyzed synthesis of Schiff base under solvent-free condition: As a green approach. *Archives of Applied Science Research*, *4*(2), 1074-1078.
25. Pal, R., Khasnobis, S., & Sarkar, T. (2013). First application of fruit juice of Citrus limon for facile and green synthesis of bis- and tris (indolyl) methanes in water. *Chemistry Journal*, *3*(1), 7-12.
26. Pal, R. (2013). Microwave-assisted eco-friendly synthesis of bis-, tris (indolyl) methanes and synthesis of di-bis (indolyl) methanes catalyzed by fruit juice of Citrus limon under solvent-free conditions. *IOSR Journal of Applied Chemistry*, *3*(4), 1-8.
27. Pal, R. (2013). New Greener Alternative for Biocondensation of Aldehydes and Indoles Using Lemon Juice: Formation of Bis-, Tris-, and Tetraindoles. *International Journal of Organic Chemistry* 3(2): 136-142.
28. Patil, S., Jadhav, S. D., & Mane, S. Y. (2011). Pineapple juice as a natural catalyst: An excellent catalyst for biginelli reaction. *International Journal of Organic Chemistry*, *1*(03), 125.
29. Patil, S., Jadhav, S. D., & Deshmukh, M. B. (2013). Eco-friendly and economic method for Knoevenagel condensation by employing natural catalyst. *Indian Journal of Chemistry, Section B*, *52*(8), 1172-1175.
30. Fonseca, A. M., Monte, F. J. Q., Maria da Conceição, F., de Mattos, M. C., Cordell, G. A., Braz-Filho, R., & Lemos, T. L. (2009). Coconut water (Cocos nucifera L.)—A new biocatalyst system for organic synthesis. *Journal of Molecular Catalysis B: Enzymatic*, *57*(1), 78-82.
31. Pal, R. (2013). A convenient, rapid and eco-friendly synthesis of bis-, tris (indolyl) methanes and synthesis of tetraindolyl compounds catalyzed by tamarind juice under microwave irradiation. *International Journal of Chemtech Applications (INTJCA) an Open Access Free Online Scientific Journal*, *2*(3), 26-40.

