JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Bottle Gourd Juice: Natural and Green Catalyst for Knoevenagel Condensation at Room Temperature

B. S. Londhe*, J. B. Gujar, N. D. Desai, A. U. Chopade, D. R. Nagargoje and R. J. Kavade
Karmaveer Bhaurao Patil Mahavidyalaya, Pandharpur, Dist. Solapur (MS), INDIA

Abstract

A simple, mild and environment-friendly protocol has been developed for Knoevenagel condensation between aromatic aldehydes and malononitrile in the presence of bottle gourd juice at room temperature. The products are obtained in excellent yields (61-95%) and are in a state of high purity. The formation of the product has been confirmed by spectral analysis (^{1}H NMR, ^{13}C NMR and HRMS) of representative compounds. This green methodology eliminates the need for hazardous basic catalysts and elevated temperatures, making it environmentally benign and industrially viable.

Keywords: Green chemistry, Knoevenagel condensation, bottle gourd juice, room temperature, natural catalyst.

1. Introduction

The **Knoevenagel condensation** is one of the most versatile and reliable carbon–carbon bond-forming reactions in organic synthesis, first described by Emil Knoevenagel in 1894 [1]. It involves the condensation of aldehydes or ketones with active methylene compounds in the presence of weak bases to form α, β-unsaturated products via enolate formation, nucleophilic addition, and elimination of water [2,3]. Due to its operational simplicity and predictable mechanism, this reaction is widely used to construct complex molecular frameworks in pharmaceuticals, dyes, agrochemicals, fragrances, and functional materials [4–6].

However, traditional Knoevenagel methods typically use bases like NaOH, KOH, or organic amines (e.g., piperidine) in volatile organic solvents such as ethanol, toluene, or benzene at elevated temperatures for prolonged times [7,8]. This raises environmental and safety concerns due to solvent toxicity, waste generation, and high energy demands [9]. Moreover, homogeneous catalysts used in these protocols are often difficult to separate and reuse, increasing costs and producing additional waste streams [10]. Harsh reaction conditions also limit substrate scope, especially for sensitive or sterically hindered compounds [11].

The green chemistry paradigm, introduced by Anastas and Warner, emphasizes designing chemical processes that reduce or eliminate hazardous substances and waste while improving efficiency [12,13]. Applying these principles to the Knoevenagel condensation has inspired alternative approaches including aqueous or solvent-free protocols, which use water as a benign medium or eliminate solvents altogether through grinding or microwave activation [14,15], heterogeneous and reusable catalysts, such as metal oxides, clays, or calcined natural materials, which simplify catalyst recovery and reuse [16,17], bio-based and agro-waste catalysts, including plant extracts, fruit ashes, or enzyme-based systems, offering biodegradable, renewable, and low-cost options [18,19], ionic liquids and deep eutectic solvents, which provide non-volatile, recyclable alternatives to traditional solvents [20,21].

Natural materials are especially promising for greener catalysis. They are biodegradable, non-toxic, abundant, and can operate under mild conditions, often containing multiple functional groups that promote catalysis without added reagents [22]. Transforming agricultural residues or plant materials into catalysts aligns well with sustainable resource use and circular economy models [23]. Bottle gourd (Lagenaria siceraria) is a widely cultivated vegetable in tropical regions, rich in water, vitamins, minerals, and various bioactive compounds [24]. Traditionally used in folk medicine, bottle gourd juice contains organic acids, amino acids, flavonoids, and saponins, which may provide catalytic activity under mild conditions [25]. Although solid plant materials and ashes have been explored, fresh plant juices remain underutilized as direct catalysts for organic synthesis [26].

The present work explores, for the first time, in continuation of our efforts [27-31] to make synthetic protocols of value-added products more and more green, the use of fresh bottle gourd juice as a natural, green catalyst for the Knoevenagel condensation at room temperature, without added solvents. This approach seeks to combine sustainability, operational simplicity, and economic viability by demonstrating Efficient catalysis under mild conditions, Minimal waste generation, Compatibility with various aldehydes and active methylene substrates and Easy work-up and potential scalability. By employing an abundant vegetable juice, this research highlights a novel method to advance sustainable synthesis, aligning with the broader goals of green chemistry and renewable catalysis [32].

2. Experimental Section

2.1 General Information

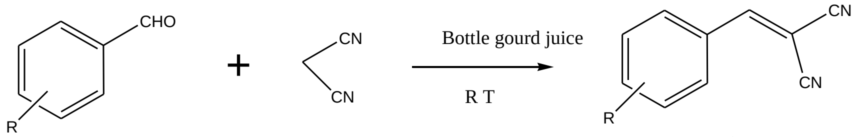
All chemicals were purchased from commercial sources and used without further purification. Melting points were recorded in open capillaries and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using DMSO-d_6 as solvent. Chemical shifts are reported in ppm relative to TMS. Reaction progress was monitored by thin-layer chromatography (TLC) using silica gel plates.

2.2 Preparation of Bottle Gourd Juice

Fresh bottle gourds were selected, washed thoroughly, and the juice was extracted using a mechanical juicer. The pH of the fresh juice was measured to be 5.2, indicating its mildly acidic in nature. The juice was used immediately without any purification.

2.3 General Procedure for Knoevenagel Condensation

Aromatic aldehydes (10 mmol), malononitrile (10 mmol), and bottle gourd juice (5 mL, pH= 5.2) were taken in a round bottomed flask and stirred at room temperature (25 °C). After half an hour, the reaction mass was suspended in water. The product formed was filtered and washed with plenty of water. The crude product thus obtained was further purified by crystallization from absolute ethanol.



1 2 3

3. Results and Discussion

3.1 Optimization Studies

The reaction conditions were optimized by varying the amount of bottle gourd juice, reaction time, and temperature. The optimal conditions were found to be 5 mL of bottle gourd juice at room temperature with 30 minutes stirring time. Increasing the catalyst amount or reaction time did not significantly improve the yields.

Table 1: Optimization for appropriate amount of bottle gourd juice [a]

Entry	bottle gourd juice (ml)	Yields (%)[b]
1	1	40
2	2	48
3	3	55
4	4	62
5	**5**	**75**
6	6	75
7	-	nd[c]

[a]Reaction conditions: p-anisaldehyde (5 mmol), malononitrile (5 mmol), at RT for 30 min.
[b]Isolated yields. [c]Reaction without bottle gourd juice.

Table 2: Optimization for appropriate reaction conditions[a]

Entry	Reaction temperature with stirring (°C)	Time	Yields (%)[b]
1	**RT**	**30 min.**	**75**
2	70	30 min.	75
3	80	30 min.	75
4	RT	15 min.	51
5	**RT**	**30 min.**	**75**
8	RT	45 min.	75

[a]Reaction conditions: p-anisaldehyde (5 mmol), malononitrile (5 mmol) in bottle gourd juice. [b]Isolated yields.

3.2 Scope and Limitations

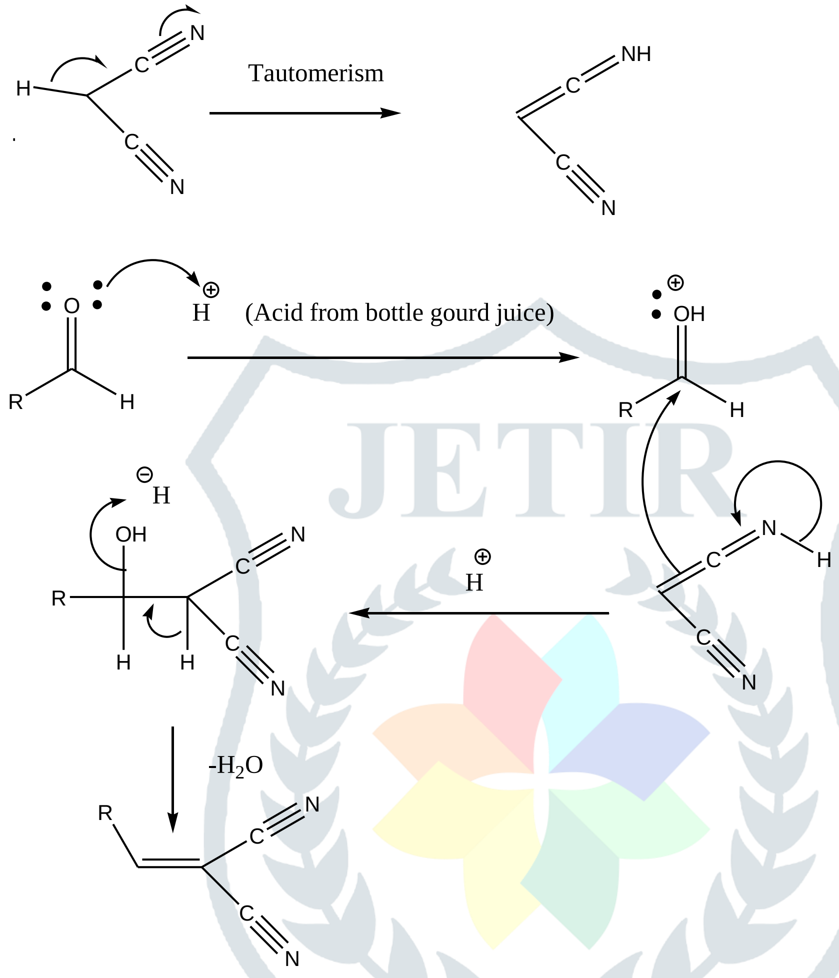
The methodology was successfully applied to various aromatic aldehydes bearing electron-donating and electron-withdrawing substituents. The results are summarized in Table 1.

Table 1. Knoevenagel Condensation of Aromatic Aldehydes with Malononitrile

Sr. No	R	Product	M. P. (°C)	% Yield
1	H	**3a**	81-82	91
2	4-OCH_3	**3b**	111-112	72
3	2-OH	**3c**	99-100	61
4	4-Br	**3d**	165-166	95
5	4-Cl	**3e**	160-161	86
6	3-Cl	**3f**	88-90	84
7	4-CH_3	**3g**	129-130	78
8	4-NO_2	**3h**	159-160	85
9	4-F	**3i**	123-124	78
10	4$N(CH_3)_2$	**3j**	183-184	88

3.3 Proposed Mechanism

The catalytic activity of bottle gourd juice can be attributed to the presence of natural acidic compounds that facilitate the protonation of the oxygen in aldehyde giving rise to electron deficient centre. The tautomerized malononitrile attacks on the electrophilic carbon of the aldehyde. Thus formed adduct leading to the desired product after elimination of water.



Proposed Mechanism for the reaction

3.4 Spectral data of a representative compounds

Compound (3b): 2-(4-methoxybenzylidene)malononitrile

^{1}H-NMR (500 MHz, $CDCl_3$): δppm= 3.91 (s, 3H, OCH_3), 7.01 (d, 2H, *J*= 10 Hz, Ar-H), 7.65 (s, 1H, CH) and 7.90 (d, 2H, *J*=10 Hz, Ar-H).

^{13}C-NMR (125 MHz, $CDCl_3$): δppm= 55.8, 115.2, 120.5, 125.7, 132.3, 132.5, 161.4, 167.9 and 168.5.

HR-ESI-MS (*m/z*): Calculated for $C_{11}H_8N_2O$ $[M+ Na]^+$: 207.0529, found : 207.0528.

5. Conclusions

A novel, environmentally benign protocol for Knoevenagel condensation has been developed using bottle gourd juice as a natural catalyst. The methodology operates under mild conditions at room temperature, providing excellent yields (61-95%) with high product purity. The process is economical, user-friendly, and suitable for industrial applications. This work demonstrates the potential of utilizing natural plant extracts as sustainable alternatives to conventional synthetic catalysts in organic transformations.

Acknowledgments

Authors acknowledges Karmaveer Bhaurao Patil Mahavidyalaya, Pandharpur, for providing research facilities.

References

1. Knoevenagel, E. Ber. Dtsch. Chem. Ges. **1894**, *27*, 2345–2346.
2. Jones, G. *Organic Reactions*; Wiley: New York, 1967; Vol. 15, pp. 204–599.
3. Freeman, J. P. *Chem. Rev.* **1980**, *80*, 329–350.
4. Tietze, L. F.; Beifuss, U. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp. 341–394.
5. Choudhary, V. R.; Tillu, V. H.; et al. *Green Chem.* **2005**, *7*, 1–4.
6. Cabello, J. A.; et al. *J. Org. Chem.* **1984**, *49*, 5195–5197.
7. Vogel, A. I.; et al. *Vogel's Textbook of Practical Organic Chemistry*; Longman: London, 1989.
8. Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*; Oxford University Press: Oxford, 2001.
9. Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686–694.
10. Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702–1706.
11. Hoz, A.; Diaz-Ortiz, A.; Moreno, A. *Chem. Soc. Rev.* **2005**, *34*, 164–178.
12. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998.
13. Anastas, P. T.; Eghbali, N. *Chem. Soc. Rev.* **2010**, *39*, 301–312.
14. Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025–1074.
15. Kaupp, G. *CrystEngComm* **2009**, *11*, 388–403.
16. Polshettiwar, V.; Varma, R. S. *Green Chem.* **2010**, *12*, 743–754.
17. Sharma, S. K.; Parikh, P. A.; Jasra, R. V. *J. Chem. Sci.* **2013**, *125*, 851–857.
18. Brahmachari, G. *Chem. Rec.* **2014**, *14*, 1–24.
19. Kour, D.; Sharma, K.; Singh, J. *Indian J. Chem.* **2013**, *52B*, 1172–1175.
20. Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2084.
21. Smith, E. L.; Abbott, A. P.; Ryder, K. S. *Chem. Rev.* **2014**, *114*, 11060–11082.
22. Sheldon, R. A. *Green Chem.* **2008**, *10*, 359–360.
23. Gallezot, P. *Chem. Soc. Rev.* **2012**, *41*, 1538–1558.
24. Heiser, C. B. *Econ. Bot.* **1979**, *33*, 346–347.
25. Ghule, B. V.; Ghante, M. H.; Saoji, A. N.; Yeole, P. G. *Indian J. Exp. Biol.* **2006**, *44*, 905–909.
26. Kour, D.; Sharma, K.; Singh, J. *Indian J. Chem.* **2013**, *52B*, 1172–1175.
27. Londhe, B. S., Gujar, J. B., Nalawade, A. M., Nalawade, R. A., & Mane, R. A. *Org. Prep. and Proc. Inter.l* **2024**. *56(4),* 371–378.
28. Londhe B. S.; Padwal S. L.; Bhosale M. R.; Mane R. A. *J. of the Iran. Chem. Soc.* **2016**, 13(3), 443-447.
29. Londhe; S B.; Pratap; R U.; Mali; R J.; Mane; A R. *Bull. of the Korean Chem. Soc.* **2010**, 31(8), 2329-2332.
30. Londhe; Shahaji B.; Khillare; Santosh; Nalawade; Rekha; Nalawade; Avinash. *J. of App. Organo. Chem.* **2021**, 1(2), 86-94.
31. Gujar; J; Londhe; B; Zambare; R; Kavade; R; Shingare; M. *Glycine: J. of App. Organo. Chem.* **2021**, 1(3), 134-142.
32. Anastas, P. T.; Bartlett, L. B.; Kirchhoff, M. M.; Williamson, T. C. *Catal. Today* **2000**, *55*, 11–22.