



## ULTRASOUND ACCELERATED GREEN OLEFINATION OF ALDEHYDES USING ZINC OXIDE NANOPARTICLE

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### Abstract

Olefination is the most important class of reaction in synthetic organic chemistry due to its wide range of applicability. Furthermore, zinc oxide nanoparticles (nano ZnO) serve as highly efficient catalysts. The current protocol offers an efficient method for the olefination of various aldehydes utilizing ZnO nanoparticles as catalysts in distilled water, providing a green reaction medium. Additionally, ultrasonication (US) is used as a green source of energy to accelerate the reaction.

**Keywords:** Ultrasonication, sonochemistry, green reaction media, nanoparticle, olefination, aldehydes, water.

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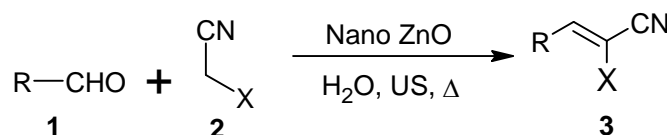
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## Introduction

Formations of olefins are the most important class of reactions since olefins are precursors of various biologically active natural and synthetic products.<sup>1</sup> In the literature, several methods and reactions have been developed for olefinations.<sup>2</sup> Some of the methods are Horner-Wadsworth-Emmons reaction, McMurry Coupling Reaction, Wittig reaction, Julia-Kocienski olefination, Tebbe olefination, Heck reaction, etc.<sup>3-9</sup> During olefination, the formation of carbon-carbon bonds is key to producing a wide variety of advanced products with great societal importance. In the literature, the Knoevenagel reaction entailed a big part of these reactions. Knoevenagel reactions are catalyzed by nitrogen-based catalysts.<sup>11</sup> These catalysts operate through different reaction conditions and paths with different reaction intermediates.<sup>12-15</sup> A simplified and greener approach to olefinations is always needed. The present protocol is a successful attempt to fill this gap using sonochemistry and

nanochemistry.<sup>16-19</sup> The application of sonochemistry or ultrasound in chemistry has wide applications in chemical transformations. It is a green technique for chemical activation and synthesis a variety of organic molecules. The most important beneficial effects of ultrasound is shorter reaction time, clean-green, and economic. Similar to sonochemistry, nanochemistry is another interesting area of research that needs to be explored, so researchers are focusing on the application of nanoparticles as nanocatalysts in organic synthesis as well as various chemical transformation reactions.<sup>20</sup> Present protocol is an efficient protocol for the olefination of various aldehydes using zinc oxide nanoparticles (nano ZnO) as a catalyst<sup>21-23</sup> in distilled water, avoiding the use of volatile organic solvents. Additionally, ultrasound (US) is used here as a green source of energy to accelerate the reaction. This protocol is operationally simple and has wide applications to generate a wide range of olefins (**Scheme 1**).



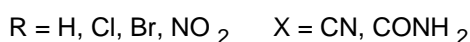
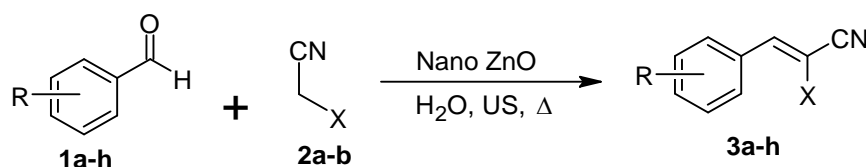
**Scheme 1:** Nano ZnO catalysed green olefination in water using US.

The chromone moiety is a subunit of various natural and synthetic bioactive molecules<sup>24-25</sup> and the chemical modification of Chromone-3-carbaldehyde scaffold is a very difficult, because, organic bases and strong acids open the pyrone ring.<sup>26-27</sup> The present protocol is effective and efficient in converting chromone-3-carbaldehyde into olefins by condensing them with active methylene compounds using nano ZnO as a catalyst in distilled water using ultrasonication.

## Results and Discussion

Zinc oxide nanoparticles (nano ZnO) is prepared by using literature chemical precipitation method (zinc acetate in absolute ethyl alcohol) and further obtained ZnO nanoparticles were characterized using spectroscopic techniques. In a pilot

experiment, aldehyde (benzaldehyde) **1a** (10 mmol), active methylene compound (malononitrile) **2a** (10 mmol), 10 ml distilled water, and a catalytic amount of ZnO nanoparticle (0.50 mmol) were sonicated at 70°C on ultrasonicator for 6 minutes, and olefine **3a** is formed with a 98% yield (**Scheme 2**). By following the above procedure, a variety of aldehydes **1a-d** were condensed with active methylene compounds (such as malononitrile and cyanoactamide) in the presence of a catalytic amount of nano ZnO (for temperature, see **Table 1**) in distilled water. Olefination time is very short, and the reaction completes in minutes and gives a variety of olefines **3a-h** in very good to excellent yields (**Scheme 2, Table 1**).



**Scheme 2:** Nano ZnO catalysed green olefination in water using US.

Here it is also observed that an increased amount of catalyst (nano ZnO) up to 1.50 mmol does not significantly change reaction time and olefins. While an amount less than 0.50 mmol nano ZnO

drastically decreased product yields and also increase reaction time, 0.50 mmol is sufficient to catalyze this green olefination reaction.

**Table 1 :** Nano ZnO catalysed green olefination in water using US.

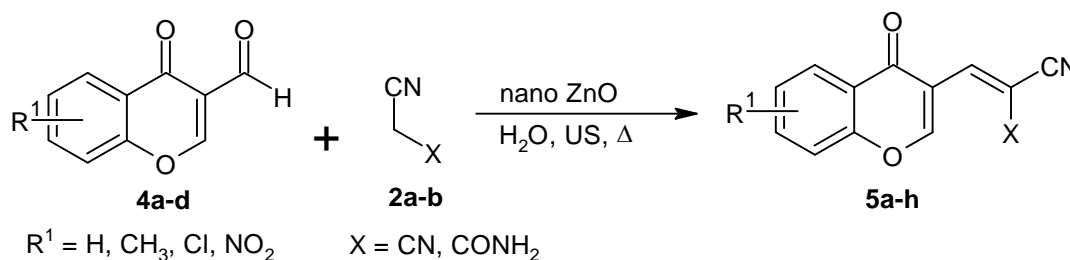
Entry	R	X	Product	Temp. °C	Time (min)	Yield (%) <sup>a</sup>
1	H	CN	<b>3a</b>	70	6	98
2	Cl	CN	<b>3b</b>	70	8	96
3	Br	CN	<b>3c</b>	75	10	94
4	NO <sub>2</sub>	CN	<b>3d</b>	75	12	93
5	H	CONH <sub>2</sub>	<b>3e</b>	75	7	97
6	Cl	CONH <sub>2</sub>	<b>3f</b>	75	9	98
7	Br	CONH <sub>2</sub>	<b>3g</b>	80	13	93
8	NO <sub>2</sub>	CONH <sub>2</sub>	<b>3h</b>	80	15	92

<sup>a</sup>Isolated yields after recrystallization.

This protocol is further applied to heterocyclic aldehydes, i.e., Chromone-3-carbaldehydes, and it was observed that this protocol is also efficient in generating olefins based on the condensation of Chromone-3-carbaldehydes (**4a-d**) and active methylene compounds (**2a-b**) (malononitrile and cyanoacetamide) in the presence of a catalytic amount of nano ZnO (for temperature see **table 2**) in distilled water to provide a variety of olefins (**5a-h**) in very good yields (**Scheme 3**).

Aromatic aldehydes **1a-h** afforded excellent yields in a comparatively shorter reaction time than

heterocyclic aldehydes **4a-d** (see **Table 1** and **Table 2**). It is also observed that heterocyclic aldehydes **4a-d** take a slightly longer reaction time to complete olefination. It is also noted that all the reactions yield selectively olefins without any side-products (**Scheme 2 and 3**). Further electron withdrawing and donating groups present on aldehydes **1a-h** as well as heterocyclic aldehydes **4a-d** do not affect the course reaction and are applicable to generate a wide range of olefins.



**Scheme 3:** Nano ZnO catalysed green olefination in water using US.

**Table 2 :** ZnO nanoparticle catalysed Knoevenagel reaction of **4** and **2**.

Entry	R <sup>1</sup>	X	Product	Temp. °C	Time (min)	Yield (%) <sup>a</sup>
1	H	CN	<b>5a</b>	75	15.0	93
2	CH <sub>3</sub>	CN	<b>5b</b>	75	18.0	94
3	Cl	CN	<b>5c</b>	75	18.0	95
4	NO <sub>2</sub>	CN	<b>5d</b>	80	20.0	92
5	H	CONH <sub>2</sub>	<b>5e</b>	80	16.0	95
6	CH <sub>3</sub>	CONH <sub>2</sub>	<b>5f</b>	80	18.0	92
7	Cl	CONH <sub>2</sub>	<b>5g</b>	80	17.0	94
8	NO <sub>2</sub>	CONH <sub>2</sub>	<b>5h</b>	80	20.0	91

<sup>a</sup>Isolated yields after recrystallization.

## Experimental Section

### General

Reagent-grade chemicals were purchased from a commercial source and used without further purification. Melting points were determined in

labotech melting point apparatus MPA350. Sonication done in a Phoenix digital ultrasonicator. Infrared (IR) spectra were recorded in KBr discs on a Perkin-Elmer 240C analyzer. <sup>1</sup>H NMR spectra were recorded on a

BRUKER AVANCE II 400 NMR spectrometer in CDCl<sub>3</sub>/DMSO-d<sub>6</sub> using tetramethylsilane (TMS) as internal standard. The progress of the reaction was monitored by thin-layer chromatography (TLC) using silica gel G (Merck). Yields refer to yield of the isolated products.

#### General procedure for the synthesis of olefines:

A mixture of aldehyde (**1a-e** or **4a-d**) (10.0 mmol), active methylene compound (**2a-b**) (10.0 mmol), nano ZnO (0.50 mmol) in 10.0 ml distilled water were sonicated at temperature (see **table 1** and **table 2**) on ultrasonicator (for appropriate time see **table 1** and **table 2**). The progress of the reaction was monitored via thin-layer chromatography. After the completion of the reaction, the reaction mass was cooled to room temperature, and the isolated olefins were filtered. The obtained products were further recrystallized in DMF:ethanol to get pure olefins. ZnO nanoparticle was isolated from the reaction mass, which was further dried in the oven at 100 °C for reuse. The obtained olefines were further confirmed by their melting points and spectral analysis data (IR, <sup>1</sup>H NMR, mass spectra).

#### Physical and spectral data of selected compounds:

p-chlorobenzylidenemalononitrile (**3b**): mp 161-162 °C; IR (KBr): 3032, 2229, 1584 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.54 (s, 1H), 8.0-7.64 (AA'BB' system, 4H).

Benzylidenecyanoacetamide (**3e**): mp 122-123°C; IR (KBr) 3401, 3165, 2219, 1693, 1597 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 8.21 (s, 1), 7.95 (d, J = 8.1, 2H), 7.85 (br d, 2H), 7.56 (m, 3H).

p-nitrobenzylidenecyanoacetamide (**3h**): mp 236-238 °C; IR (KBr): 3438, 3197, 2225, 1692, 1600 cm<sup>-1</sup>; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 8.3 (AA'BB' system, 4H), 8.32 (s, 1H), 8.10-7.90 (br d, 1H).

[(4-oxo-4*H*-chromen-3-yl)methylidene]propanedinitrile (**5a**): mp: 217-218 °C; IR (KBr): 3076,3028, 2225, 1649, 1590, 1458 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 8.17-7.49 (m, 4H, ArH), 8.01 (s, 1H), 9.06 (s, 1H); Mass (*m/z*): 222 (M<sup>+</sup>).

[(6-chloro-4-oxo-4*H*-chromen-3-yl)methylidene]propanedinitrile (**5c**): mp: 206-208 °C; IR (KBr): 3170,3031, 2227, 1660, 1609, 1553, 1465 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 8.11-7.72 (m, 3H), 8.20 (s, 1H), 9.12 (s, 1H); Mass (*m/z*): 256 (M<sup>+</sup>).

(2*Z*)-2-cyano-3-(4-oxo-4*H*-chromen-3-yl)prop-2-enamide (**5e**): mp: 201-202 °C; IR (KBr): 3399, 3168, 3060, 2227, 1681, 1628, 1561, 1460 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.63 (br-s, 1H, N-H), 7.75

(br-s, 1H, N-H), 8.13-7.44 (m, 4H, Ar-H), 8.25 (s, 1H), 9.00 (s, 1H); Mass (*m/z*): 240 (M<sup>+</sup>).

(2*Z*)-3-(6-chloro-4-oxo-4*H*-chromen-3-yl)-2-cyanoprop-2-enamide (**5g**): mp: 219-220 °C.

IR (KBr): 3402, 3312, 3190, 3036, 2799, 2213, 1686, 1658, 1591, 1464 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 7.51 (br-s, 1H, N-H), 7.59 (br-s, 1H, N-H), 8.07-7.56 (m, 3H, Ar-H), 8.26 (s, 1H), 8.97 (s, 1H); Mass (*m/z*): 274 (M<sup>+</sup>).

#### Conclusion

In summary, we have developed a green, simple, and rapid protocol for the synthesis of olefins via condensation of aldehydes (aromatic and heterocyclic) with active methylene compounds (malononitrile and cyanoacetamide) using nano ZnO (zinc oxide) as an efficient catalyst. Another merit of this procedure is the avoidance of volatile organic solvents and the use of distilled water as a green solvent. A variety of aldehydes (aromatic and heterocyclic) is employed here. Nano ZnO has shown excellent catalytic activity for this protocol and generates olefins without forming any by-products. Using ultrasonication, shorter reaction times, and very good to excellent yields are other merits of this procedure. Further catalysts can be recovered and reused without purification. In short, this procedure is highly efficient in generating olefins using green reaction media and green source of energy.

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#### References

- Liu, J.; Liu, X.; Wu, J.; Li, C.-C. Total Synthesis of Natural Products Containing a Bridgehead Double Bond. *Chem* **2020**, *6* (3), 579-615. [https://doi.org/10.1016/j.chempr.2019.12.027]
- Salvado, O.; Fernández, E. A Modular Olefination Reaction between Aldehydes and Diborylsilylmethide Lithium Salts. *Chem. Commun.* **2021**, *57*, 6300-6303. [https://doi.org/10.1039/D1CC01882E].
- Julia, M.; Kocienski, P. J. Olefination of Carbonyl Compounds: The Julia-Kocienski Reaction. *J. Chem. Soc., Chem. Commun.* **1975**, (16), 657-658. DOI: [10.1039/c3975000657].

4. Scott, W. J.; McMurry, J. E. Olefin Synthesis via Organometallic Coupling Reactions of Enol Triflates. *Acc. Chem. Res.* **1988**, 21 (2), 47–54. [https://doi.org/10.1021/ar00146a001].
5. Reichwein, J. F.; Pagenkopf, B. L. A New Horner–Wadsworth–Emmons Type Coupling Reaction between Nonstabilized  $\beta$ -Hydroxy Phosphonates and Aldehydes or Ketones. *J. Am. Chem. Soc.* **2003**, 125 (7), 1821–1824. [https://doi.org/10.1021/ja027658s].
6. Niyomchon, S.; Oppedisano, A.; Aillard, P.; Maulide, N. A Three-Membered Ring Approach to Carbonyl Olefination. *Nat. Commun.* **2017**, 8 (1), 1091. [https://doi.org/10.1038/s41467-017-01036-y].
7. Sim, J.; Jang, E.; Kim, H.J.; Jeon, H. Total Syntheses of Pladienolide-Derived Spliceosome Modulators. *Molecules* **2021**, 26, 5938. [https://doi.org/10.3390/molecules26195938].
8. Soorukram, D.; Pohmakotr, M.; Kuhakarn, C.; Reutrakul, V. Stereoselective Synthesis of Tetrahydrofuran Lignans. *Synthesis* **2018**, 50 (24), 4746–4764. [https://doi.org/10.1055/s-0037-1610289].
9. Landge, V. G.; Babu, R.; Yadav, V.; Subaramanian, M.; Gupta, V.; Balaraman, E. Iron-Catalyzed Direct Julia-Type Olefination of Alcohols. *J. Org. Chem.* **2020**, 85 (15), 9876–9886. [https://doi.org/10.1021/acs.joc.0c01173].
10. Maryanoff, B. E.; Reitz, A. B. The Wittig Olefination Reaction and Modifications Involving Phosphoryl-Stabilized Carbanions: Stereochemistry, Mechanism, and Selected Synthetic Aspects. *Chem. Rev.* **1989**, 89 (4), 863–927. [https://doi.org/10.1021/cr00094a007].
11. Van Beurden, K.; de Koning, S.; Molendijk, D.; van Schijndel, J. The Knoevenagel Reaction: A Review of the Unfinished Treasure Map to Forming Carbon–Carbon Bonds. *Green Chem. Lett. Rev.* **2020**, 13 (4), 349–364. [https://doi.org/10.1080/17518253.2020.1851398].
12. Nenajdenko, V. G.; Varseev, G. N.; Shastin, A. V.; Balenkova, E. S. The Catalytic Olefination Reaction of Aldehydes and Ketones with  $\text{CBr}_3\text{CF}_3$ . *J. Fluorine Chem.* **2005**, 126 (6), 907–913. [https://doi.org/10.1016/j.jfluchem.2005.03.020].
13. Lin, Y.-M.; Li, Z.; Casarotto, V.; Ehrmantraut, J.; Nguyen, A. N. A Catalytic, Highly Stereoselective Aldehyde Olefination Reaction. *Tetrahedron Lett.* **2007**, 48 (31), 5531–5534. [https://doi.org/10.1016/j.tetlet.2007.05.163].
14. Ventura, D. L.; Heller, S. J.; Noworyta, T. D.; Kijanka, K. C.; Belz, B. M. Metallophthalocyanine Catalyzed Olefination of Aldehydes. *Tetrahedron Lett.* **2019**, 60 (3), 302–305. [https://doi.org/10.1016/j.tetlet.2018.12.039].
15. Muzalevskiy, V. M.; Shastin, A. V.; Shikhaliev, N. G.; Magerramov, A. M.; Teymurova, A. N.; Nenajdenko, V. G. Ionic Liquids as a Reusable Media for Copper Catalysis: Green Access to Alkenes Using Catalytic Olefination Reaction. *Tetrahedron* **2016**, 72 (45), 7159–7163. [https://doi.org/10.1016/j.tet.2016.09.050].
16. Puri, S.; Parmar, A.; Chopra, H. K. Ultrasound Assisted Reactions. In *Handbook of Greener Synthesis of Nanomaterials and Compounds*; Kharisov, B., Kharissova, O., Eds.; Elsevier, **2021**; pp 177–246. [https://doi.org/10.1016/B978-0-12-821938-6.00006-2].
17. Bonrath, W. Ultrasound Supported Catalysis. *Ultrasonics Sonochem.* **2005**, 12 (1–2), 103–106. [https://doi.org/10.1016/j.ultsonch.2004.03.008].
18. Chaturvedi, S.; Dave, P. N. Nanocatalyst: As Green Catalyst. In *Handbook of Greener Synthesis of Nanomaterials and Compounds*; Kharisov, B., Kharissova, O., Eds.; Elsevier, **2021**; pp 445–458. [https://doi.org/10.1016/B978-0-12-821938-6.00013-X].
19. Amaniampong, P. N.; Jérôme, F. Catalysis under Ultrasonic Irradiation: A Sound Synergy. *Curr. Opin. Green Sustain. Chem.* **2020**, 22, 7–12. [https://doi.org/10.1016/j.cogsc.2019.11.002].
20. Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H.; Bouhrara, M.; Basset, J.-M. Magnetically Recoverable Nanocatalysts. *Chem. Rev.* **2011**, 111(5), 3036–3075. DOI: [10.1021/cr1002459].
21. Wang, H.; Zhang, L.; Chen, Z. Nanostructured ZnO Catalysts for Hydrogenation Reactions. *J. Phys. Chem. B* **2019**, 123, 4567–4575.
22. Li, X.; Liu, S.; Wu, Q. Enhanced Catalytic Activity of ZnO Nanoparticles in Organic Synthesis. *J. Catal.* **2018**, 345, 123–135.
23. Chen, Q.; Wang, Y.; Zhang, J. Tailoring ZnO Nanorods as Highly Active Catalysts for Selective Oxidation Reactions. *ACS Appl. Mater. Interfaces* **2016**, 8, 12345–12356.
24. Kumar, A.; Sharma, P. P.; Kaur, R.; Kumar, N.; Sharma, M. Chromone: A Privileged Structure in Medicinal Chemistry. *Chem. Biol.*

- Lett. **2020**, 7(3), 125-140. DOI: [10.1007/s13588-020-00278-0].
24. Huang, X.; Li, X.; Xue, Y.; Zhu, X. Recent Advances in the Chemical Synthesis and Biological Activities of Chromone Derivatives. *Curr. Org. Synth.* **2017**, 14(2), 188-203. DOI: [10.2174/1570179413666160810122714].
25. Mallaiah, V.; Murthy, P. S.; Narsimhulu, G.; Pasha, M. A. Chemical Modification of Chromone-3-carbaldehyde: Challenges and Opportunities. *Curr. Org. Chem.* **2020**, 24(22), 2664-2681. DOI: [10.2174/1385272823666201015095258].
26. Gupta, R.; Chauhan, P. M. S. Synthetic Strategies for Functionalization of Chromone Scaffold: A Comprehensive Review. *Eur. J. Med. Chem.* **2021**, 210, 112967. DOI: [10.1016/j.ejmech.2020.112967].