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COMPARISON OF CONVENTIONAL, MICROWAVE AND GRINDING TECHNIQUES FOR SYNTHESIS OF BENZ-AZOLES

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Abstract: *This article involves comparative study of benzoxazoles/ benzimidazoles achieved by cyclocondensation reaction between o-aminophenol/o-phenylenediamine and variety of aryl aldehydes under solvent free condition by employing different techniques i.e. microwave irradiation heating, conventional heating and mortar pestle grinding technique. Comparison of physical constant, yield and reaction time of titled compounds are discussed based on different form of transformation of energy to the reaction mixture. The characterisation techniques IR and ^{1}H-NMR fully supported the structures of synthesized benzoxazoles/ benzimidazoles.*

Keywords: *Microwave heating, grinding technique, benzoxazoles, benzimidazoles.*

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INTRODUCTION

Microwave irradiation technique for different types of organic reactions has been well established as an environmentally friendly synthesis[1] and has recently been reviewed[2], as an efficient to prepare library of compounds very fast with high purity and better yields. Microwave heating technique provides a number of advantages over the standard heating technique[3]. High density microwave irradiation involves electromagnetic waves, heat the entire volume at about same rate and therefore useful for accelerating time consuming reactions[4] and in conventional heating, surface of material heat first and then heat moves inward[5].

Grinding technique is one which has been increasingly used in organic synthesis compared to conventional methods[6, 7]. The work reported by Toda on successful reactions by grinding attracted the attention of chemist that many reactions could be conducted in high yield by just grinding solid-solid or solid-liquid together[8]. Article literature revealed that in grinding the reaction is initiated with the transfer of small amounts of friction energy[9]. The reactions proceeds are exothermic, grinding reaction would not work out to get desire product if the reaction is endothermic in nature.

Benzoxazoles, benzimidazoles are important structural motifs exhibiting remarkable activities due to slight modification in the substitution pattern both the ring causes distinguishable difference in their pharmacological activities[10-13]. Benzimidazole ring having lower toxicity and high stability used as corrosion inhibitors for N80 steel-15% HCl system[14].

The present article focuses on comparison of physical constant, yield and reaction time of 2-aryl-benzoxazoles/benzimidazoles obtained via cyclisation of o-aminophenol/o-phenylenediamine with aromatic aldehydes employing microwave, conventional and hand grinding method under solvent free condition considering different form of transformation of energy to the reaction.

Result and Discussion

Melting points were uncorrected and recorded using digital melting point apparatus (Veego-DMP). All chemicals used were of A. R. grade. IR spectra were recorded on a Shimadzu spectrophotometer in the range 4000-400cm^{-1} using KBr pellets. ^{1}H-NMR spectra were obtained on a Bruker Avance II spectrophotometer in DMSO-d^{6}. Chemical shifts were obtained in ppm (δ) and were measured using TMS as reference. Purity of the compounds was checked on silica gel-G plates by thin layer chromatography. The cyclocondensation between aryl aldehydes and o-aminophenol/o-phenylenediamine leads to afford 2-aryl-benzoxazoles/benzimidazoles using microwave, conventional and hand grinding method in good to excellent yield. The reactions were performed in domestic microwave oven at 800 W and by liquid assisted hand grinding in mortar pestle. On comparison of physical constant, yield

and reaction time of representative products. The different form of transformation of energy to the reaction mixture taken into account with significance of this work is very small mechanochemical agitation was found to be enough for initiating such condensation reaction rather to use thermal energy or microwave energy.

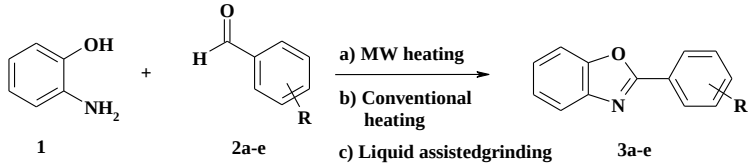
Experimental Procedure

Synthesis of 2-aryl-benzoxazoles (3a-e) and 2-aryl-benzimidazoles (3f-i)

a) Microwave heating method: A mixture of o-aminophenol **(1)** (0.2 mol) and various aryl aldehydes **(2a-e)** (0.2 mol) irradiated under microwave condition for 3-4 min. A solid mass obtained was washed with water, dried, recrystalised in ethyl acetate and identified as a 2-aryl benzoxazoles (**3a-e**).

b) Conventional heating method: A cyclocondensation reaction of o-aminophenol **(1)** and aryl aldehydes **(2a-e)** in solvent free condition refluxing for 3-4 hr leads to afford solid mass, recrystalised in ethyl acetate and identified as a 2-aryl benzoxazoles (**3a-e**).

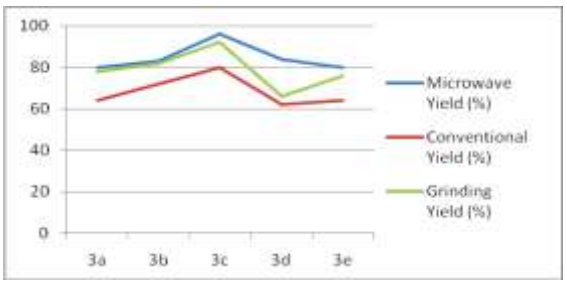
c) Grinding method: A mixture of o-aminophenol **(1)** and aryl aldehydes **(2a-e)** was ground in a mortar with pestle at room temperature for 15-20 min. A solid mass obtained was washed with water, dried, recrystalised in ethyl acetate results 2-aryl benzoxazoles (**3a-e**). Compound (**3a**): Anal. Calcd. for C13H9NO, Calculated : C 79.98 , H 4.65 , N 7.17, Found : C 78.91, H 4.62, N 6.97. IR (KBr) cm^{-1}, 3018 (Aro-CH), 1624 (C=N), 1483 (C=C). ^{1}H-NMR (DMSO-d6) ppm, 7.08-7.17 (s, 5H, Ar-H), 6.81-6.92 (m, 4H, Benzox-H).

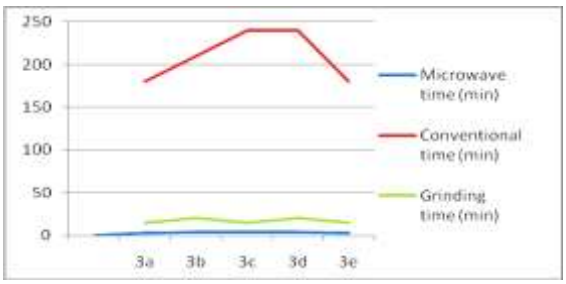


Where, 3a-e, R = H, *o*-hydroxy, *o*-nitro, *p*-methoxy, *p*-chloro,

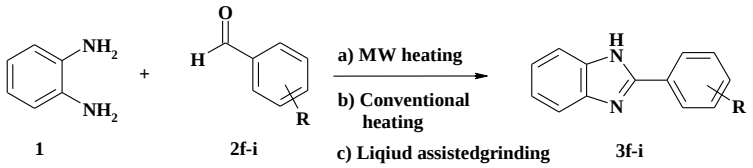
Comparison data of 2-aryl-benzoxazoles (3a-e) using different techniques (Scheme 1)

Technique	Microwave			Conventional			Grinding		
Compounds	Yield (%)	m. p. (^{0}C)	time (min)	Yield (%)	m. p. (^{0}C)	time (min)	Yield (%)	m. p. (^{0}C)	time (min)
3a	80	172	3	64	172	180	78	171	15
3b	83	154	4	72	156	210	82	154	20
3c	96	190	4	80	192	240	92	188	15
3d	84	184	4	62	184	240	66	182	20
3e	80	122	3	64	120	180	76	122	15





Similarly 2-aryl-benzimidazoles (**3f-i**) were achieved by using 1, 2-diaminobenzene (**1**) and aryl aldehydes (**2f-i**) by employing above methods. Compound (**3f**): Anal. Calcd. for C13H10N2, Calculated : C 80.39 , H 5.19 , N 14.42, Found : C 77.86, H 5.03, N 14.98. IR (KBr) cm^{-1}, 3363 (-NH), 3053 (Aro-CH), 1454 (C=C). ^{1}H-NMR (DMSO-d6) ppm, 7.71-7.83 (m, 4H, Benzmid-H), 7.31-7.65 (m, 4H, Ar-H), 8.83 (s, 1H, NH) (Scheme 2).

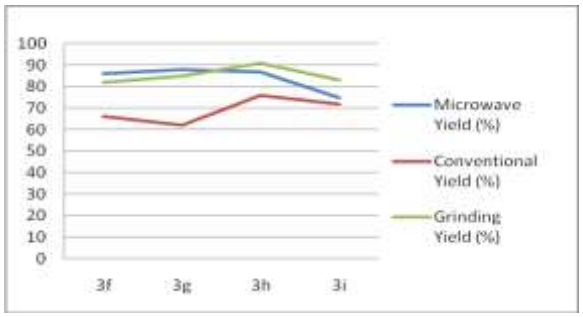


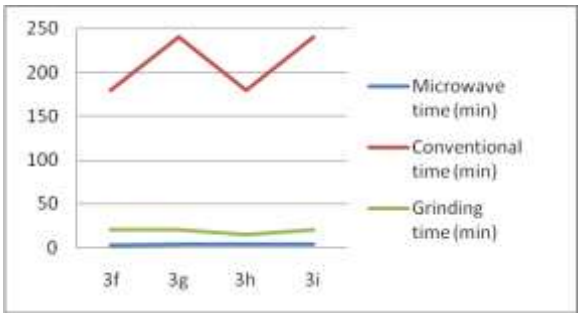
1 2f-i 3f-i

Where, 3f-i, R = H, *o*-hydroxy, *o*-nitro, *p*-methoxy

Comparison data of 2-aryl-benzimidazoles (3f-i) using different techniques (Scheme 2)

Technique	Microwave			Conventional			Grinding		
Compounds	Yield (%)	m. p. (^{0}C)	time (min)	Yield (%)	m. p. (^{0}C)	time (min)	Yield (%)	m. p. (^{0}C)	time (min)
3f	86	294	3	66	293	180	82	294	20
3g	88	176	4	62	172	240	85	175	20
3h	87	238	4	76	242	180	91	241	15
3i	75	224	4	72	223	240	83	224	20





CONCLUSION

The different form of energy used in microwave irradiation, conventional heating and hand grinding method which transforms substrate into product were discussed and efficient, versatile and inexpensive mechanochemical route for condensation reaction or can be applicable for cyclization reaction developed which involves comparative study of synthesis of benzoxazoles/ benzimidazoles by cyclocondensation reaction by employing microwave, conventional and simple mortar pestle hand grinding method. The mild reaction conditions and proceeds just by grinding the substrates without any solvent and hence match the green chemistry protocols. In addition to this remarkable feature of this work is very small mechanochemical agitation was found to be enough for initiating such condensation reaction rather to use thermal energy or microwave energy.

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REFERENCES

1 Oliver K, *Angew Chem Int Ed*, 43 (2004) 6250.
2 Oliver K & Doris D, *Nature Reviews Drug Discovery*, 5 (2006) 51
3 Lindstrom P, Tierney J, Wathley B & Westman J, *Tetrahedron*, 57 (2001) 9225.
4 Gronnow M J, White R J, Clark J H & Macquarrie D J, *Org Process Res Dev*, 9 (2005) 516.
5 Sekhon B S, *Int J Pharm Tech Res*, 2(1) (2010) 828.
6 Toda F, *Synlett*, 303 (1993) 312.
7 Desiraju G R, *Organic Solid State Chemistry*, (Elsevier Science Publishers, Amsterdam) 1987 550.
8 Toda F, Tanaka K & Sekikawa A, *J Chem Soc*, *Chem Commun*, 1987 279.
9 Tanaka K, *Solvent-free Organic Synthesis*, 2nd edn (Wiley-VCH, Verlag GmbH & Co Weinheim) 2009 33.
10 Nishida A, Fuwa M, Naruto S, Sugano Y, Saito H & Nakagawa M, *Tetrahedron Lett*, 41 (2000) 4791.
11 Kohli P & Shrivastava S D, *J Chinese Chem Soc*, 54 (2007) 1003.
12 Baltorka M, Moghadama M, Tangestaninjada S & Mirkhania V, *J Iran Chem Soc*, 5 (2008) S65-S70.
13 Aslam Z, Kaplancikli, Gulham, Zitouni T, Revial G & Guven K, *Arch Pharm Res*, (27)11 (2004) 1081-1085.

14 Yadav M, Yadav P N & Sharma U, *Ind J Chem Tech*, 20 (2013) 363.