National Conference on New Trends in Green Chemistry and Environmental Science
In Association with International Journal of Scientific Research in Science and Technology
Volume 9 | Issue 8 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)

Synthesis of 2,4,5-triarylimidazoles Catalyzed by Ni nps/ stilbite Zeolite

L. S. Gadekar
Chemistry Research Centre, Vasantdada Paatil College Patoda, Dist. Beed, Maharashtra, India

ABSTRACT

Ni nps/stilbite shows promising results in various schemes of organic transformation. In the present research article, 2,4,5-triarylimidazoles are synthesized by refluxing benzil or benzoin, aromatic aldehyde, ammonium acetate and small amount of Ni nps/stilbite stilbite for appropriate time to get expected product. The reaction process was very simple. More yield and reusable catalyst are the benefit of present scheme.

Keywords: Green chemistry, designing safer chemicals, sustainable development.

I. INTRODUCTION

Nitrogen structured imidazole nucleus and there derivatives are found to possess a broad range of biological activities. They are well known as inhibitors of P38MAP kinase [1], fungicides, herbicides [2], anti-inflammatory [3], antithrombotic [4], growth regulators in plant [5] and as a therapeutic agents [6]. In addition, they are used as photosensitive compounds in photography [7]. Some substituted triarylimidazole are selective antagonists of the glucagons receptor [8] and inhibitors of IL-1 biosynthesis [9], also evaluated for cyclooxygenase-2(COX-2) inhibitory activity [10] and α-glocosidase inhibitory activity [11].

In 1882, First synthesis of the imidazole core starting from 1,2-dicarbonyl compounds, aldehydes and ammonia, to obtain 2,4,5-triphenylimidazole proposed by Radziszewski and Jaap [12]. Grimmett and et al proposed the synthesis of the imidazole using nitriles and esters [13]. Literature survey reveals several methods for the synthesis of many substituents for 2,4,5-triarylimidazoles using $ZrCl_4$ [14], zeolites HY/silica gel [15], $NaHSO_3$ [16], sulphanilic acid [17], SiO_2-$NaHSO_4$ [18], iodine [19], ceric ammonium nitrate [20], oxalic acid [21], ionic liquid [22] and also by microwave irradiation using acetic acid [23]. However, many of these procedures suffer from harsh reaction conditions, low yield, difficulties in work-up and relatively expensive reagents. Thus, a simple, general and efficient procedure is still in demand for the synthesis of 2,4,5-triarylimidazole derivatives via multi-component reaction. Moreover, there are relatively limited number of reports on the synthesis of 2,4,5-triarylimidazoles. Consequently, there is scope for work in preparing variations of the substituents in the product, mild conditions and better yields. Herein, we report a simple method for the synthesis of 2,4,5-triarylimidazoles using Ni nps/ stilbite zeolite [24] as a catalyst.

Experimental

All chemicals are purchased from Aldrich, Rankem and s.d. fine chemicals limited and used as received without purification. The melting points of the compounds were taken in an open capillary in a paraffin bath. IR spectra were recorded on a Jasco FTIR-4100 spectrophotometer. ^{1}H NMR spectra were recorded on an 80 MHz FT-NMR spectrometer in $CDCl_3$ as a solvent and chemical shift values are recorded in units δ (ppm) relative to tetramethylsilane (Me_4Si) as an internal standard.

General procedure for synthesis of 2,4,5-triarylimiazole derivatives

A mixture of benzil or benzoin (5 mmol), aromatic aldehyde (5 mmol), ammonium acetate (10 mmol) and Ni nps/ stilbite (1 wt% with respect to initial concentration of reactant) was refluxed in ethanol (15 mL) in a round bottom flask, for the time as mentioned in Table 2. The reaction was monitored by TLC using alumna foil. After completion of reaction, the reaction mixture was poured into crushed ice and the solid product is formed, was filtered and recrystallized from ethanol to obtain pure products.

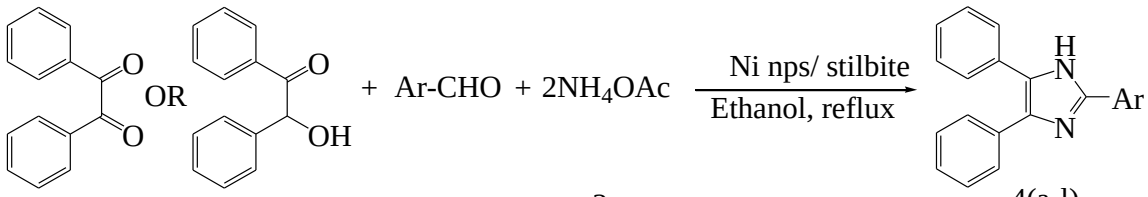
Spectroscopic data

2,4,5-Triphenyl-1*H*-imidazole **(4a).** IR (KBr, cm^{-1}): 3451 (N-H), 3053 (C-H), 1602 (C=C), 1575 (C=N). ^{1}H NMR ($CDCl_3$, 80 MHz,δ,ppm) : 7.16-8.00 (m, 15H, Ph), 9.21 (br s, NH).

EIMS (m/z, %): 297 (M+1).

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole **(4c).** IR (KBr, cm^{-1}): 3451 (N-H), 1603 (C=C), 1583 (C=N). ^{1}H NMR ($CDCl_3$,80 MHz,δ,ppm):7.12-7.60 (m, 10H, Ph), 7.36 (d, 2H, J =10 Hz, Ar), 7.82 (d, 2H, J =10 Hz, Ar).

EIMS (m/z, %): 331 (M+1).



1 2(a-l) 3 4(a-l)

Scheme 1

Table 1. Optimization of reaction conditions and wt% of Ni nps/ stilbite for the synthesis of 2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole.

Solvent	Wt (%) of catalyst	Reaction time (min)	Yield(%)[a]
Water	0.5	30	54
Acetonitrile	0.5	30	72
Acetonirile-water (1:1)	0.5	30	66
Ethanol	0.5	30	93
Ethanol-water (1:1)	0.5	30	81
Ethanol	1	30	97
Ethanol	1.5	30	82

[a]All yield refers to isolated products

Table 2. Synthesis of 2,4,5-triaryl-1*H*-imidazole derivatives using benzil or benzoin, ammonium acetate, aromatic aldehydes, and 1 wt% Ni nps/ stilbite zeolite.

Entry	Ar	Time(min)		Yield (%)[a,b]		M.P. in °C
		Benzil	Benzoin	Benzil	Benzoin	Found
4a	C_6H_5	25	40	97	96	273-275
4b	2-ClC_6H_4	35	45	96	94	195-196
4c	4-ClC_6H_4	20	35	97	97	259-260
4d	4-MeC_6H_4	35	40	93	96	230-231
4e	4-$OMeC_6H_4$	35	35	93	95	228-229
4f	3,4-$(OMe)_2C_6H_3$	30	45	95	92	220-222
4g	4-$NO_2C_6H_4$	25	50	96	95	233-234
4h	4-$N(Me)_2C_6H_4$	20	40	97	95	250-261
4i	4-OHC_6H_4	25	45	95	91	266-267
4k	4-FC_6H_4	30	50	95	92	191-192
4l	2-Furyl	40	45	94	93	198-200

[a]All yield refers to isolated products. [b]-all compounds are known and spectral data matched with authentic data.

Table 3. Reusability of the catalyst for 4c (Table 2).

Entry	Cycle	Yield (%)[a]
1	Fresh	97
2	First	96
3	Second	95
4	Third	95

[a]Yield refers to isolated product.

Results and discussion

Initially, we studied the catalytic efficiency of Ni nps/ stilbite for synthesis of 2-(4-chlorophenyl)-4,5-diphenyl-1*H*-imidazole **(4c)** using 1: 1: 2 ratio of benzil, ammonium acetate and 4-chlorobenzaldehyde in different solvents and various wt% of Ni nps/ stilbite zeolite catalyst with respective to initial concentration of reactant (Scheme 1). The compound **4c** was isolated with 97% yield using optimized reaction condition (Table 1), in ethanol and 1 wt% Ni nps/ stilbite. Using the optimized reaction conditions, a range of 2,4,5-triarylimidazole derivatives were synthesized and results are summarized in Table 2.

The results of above synthetic route are inspiring. In a similar manner a variety of derivatives were synthesized using different substitute of aromatic aldehydes and in each case it is observed that the time period of synthesis was reduced considerably and the yield of the products changed to excellent yields. It is interesting to note that the nature of substituent (o-, m-, p-) on the aromatic ring does not affect on the yield of products. The reactions of various aromatic aldehydes substituent carrying electron-donating or electron-withdrawing groups were also successfully carried out with present method. The solvent play a vital role in the transformation, solvent free reaction is best, but if it needs solvent it should be water, which is universal solvent also, non-toxic, non-inflammable, inexpensive and abundantly available. But use of water in this reaction gave only moderate yield of product (54%). So we studied the effect of different solvents in the synthesis of 2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (4c) and results are summarized in Table 1. Among them ethanol was found to be the most efficient with respect to shorter reaction time and maximum yield of product (97%).

To determine the role of catalyst, the same reaction was carried out in the absence of catalyst, which resulted in very less product formation (36%), after 90 min. These results indicate that catalyst exhibit a high catalytic activity in this transformation due to its larger surface area. The reusability of the catalyst is important for all aspects to decrease the cost of material which is being prepared. Therefore the recovery and reusability of catalyst was examined. The catalyst was separated and reused after washing it with n-hexane and drying at 80^{o}C in the synthesis of 2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (4c) and it was found that the catalyst shows good results with four successive reaction (Table 3).

This procedure has offers several advantages i.e. increased variations of substituents in the product with high yields, operational simplicity, minimum environmental effects and above all, the ease in purification of products simply by recrystallization.

Conclusion

In conclusion, we have developed a convenient and efficient protocol for one pot synthesis of 2,4,5-triarylimidazoles by three component coupling reactions of benzil or benzoin, aldehydes and ammonium acetate in the presence of Ni nps/ stilbite zeolite as a catalyst in ethanol solvent. The method is associated with several advantages such as simple experimental procedure, utilisation of heterogeneous catalyst, short reaction times, excellent yields and reusability of the catalyst. We feel the method will find important applications for the synthesis of 2,4,5-triarylimidazoles.

II. REFERENCES

[1]. PJ.C. Lee, P.R. Young, et al., Nature, 372 (1994) 739.
[2]. T. Maier, R. Schmierer, K. Bauer, H. Bieringer and B. Sachse., US Patent, 4820335 (1989): Chem Abstr., 111 (1989) 19494.
[3]. J. G. Lombardino and E.H. Wiseman, J. Med Chem., 17 (1974) 1182.
[4]. A. P. Phillips, H. L. White and S. Rosen., Eur Pat Appl EP, 58 (1982) 890.

[5]. R. Schmierer, H. Mildenberger and H. Buerstell., German Patent, 361464 (1987); Chem Abstr., 108 (1988) 37838.
[6]. J. Heeres, L. J. J. Backx, J.H. Mostmans and J. Vancustem., J. Med. Chem., 22(8) (1979) 1003.
[7]. I. Satoru, Imidazoles derivative for chemiluminescence microanalysis., Japan Kokkai Tokyo Koho JP, 01, 117, 867, May 10 (1989); Chem. Abstr., 111, (1989) 214482.
[8]. L. L. Chang, K. L. Sidler and M. A. Cascieri, Biorg. Med. Chem. Lett., 11 (2001) 2549.
[9]. T. F. Gallagher, S. M. Fier-Thompson and R. S. Garigipati, Biorg. Med. Chem. Lett., 5 (1995) 1171.
[10]. A. Zarghi, S. Arfaei, R. Ghodsi, Medicinal Chemistry Research, 21 (2012) 1803.
[11]. G.Wang, Z. Peng, J. Wang, J. Li, X. Li, Bioorg. Med. Chem. Lett., 26(13) (2016) 5719.
[12]. F. Japp and H. Robinson, Chem. Ber., 15 (1882) 1268.
[13]. M. Grimmett, A. Katritzky, C. Rees and E. Scriven, Pergamon: NewYork, 3 (1996) 77.
[14]. G. Sharma, Y. Jyothi and P. Lakshmi., Synth. Commu., 36 (2006) 2991.
[15]. S. Balalaie, A. Arabanian and M. Hashtroudi, Mont. Fur. Chemie., 131 (2000) 945.
[16]. J. Sangshetti, N. Kokare, A. Kotharkar and D. Shinde, Mont. Fur. Chemie., 139 (2008) 125.
[17]. A. Mohammed, N. Lokare, J. Sangshetti and D. Shinde, J. Korean Chem. Soc., 51 (2007) 418.
[18]. F. Hatamjafari, H. Khojastehkouhi, Orient. J. Chem., 30(1) (2014) 329.
[19]. M. Kidwai, P. Mothsra, V. Bansal and R. Goyal., Mont. Fur. Chemie., 137 (2006) 1189.
[20]. J. N. Sangshetti, N. D. Kakare, S. A. Kotharkar and D. B. Shinde, J. Chem. Sci., 120(5) (2008) 463.
[21]. N. D. Kokare, J. N. Sangshetti and D. B. Shinde, Synthesis, (2007) 2829.
[22]. S. Siddiqui, U. Narkhede, S. Palimkar, T. Daniel, R. Lahoti and K. Srinivasan, Tetrahedron, 61 (2005) 3539.
[23]. J. F. Zhou, Y. Z. Song, Y. L. Zhu and S. J. Tu, Synth. Commun., 35 (2005) 1369.
[24]. L. Gadekar, S. Katkar, K. Vidhate, J. Biol. Chem. Chron. 2019, 5(3), 83.