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Research Article

AN EFFICIENT SYNTHESIS OF 2,4,5-TRIARYL-1*H*-IMIDAZOLE USING SnO_2/SiO_2 NANOCOMPOSITE CATALYST

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ABSTRACT

SnO2/SiO2 catalyzed synthesis of 2,4,5-triarylimidazoles by the condensation of benzoin, aromatic aldehydes and ammonium acetate in presence of ethanol as solvent. The synthesis highlights a synthesis and use of SnO2/SiO2 nanocomposite heterogeneous catalyst and its reusability. The method is cost effective and ecofriendly. And use of ethanol as a solvent makes the method more green and efficient. The method has simple workup procedure and the products are obtained in good to moderate yields.

KEYWORDS: 2,4,5-triarylimidazoles, heterogeneous catalyst, SnO2/SiO2, benzoin.

INTRODUCTION

Imidazole ring system is an important nucleus found in a huge number of natural products and pharmacologically active compounds like Omeprazole[1], Trifenagrel[2], Benzodiazepine[3] and the Cimetidine[4] are imidazole derivatives. Recently 2,4,5-Triaryl-1*H*-imidazole compounds are gaining considerable significance because of their large spread biological activities and also their use has been increased in synthetic chemistry. Imidazole ring are largely used in ionic liquids. Owing to such a huge importance of imidazole many methods for the synthesis of imidazole have been reported [5-7]. Radziszewski and Japp in 1882, synthesized imidazole for first time by reacting 1,2-dicarbonyl compound, a variety of aldehydes and ammonia[8]. In recent literature many method are been reported using benzil/benzoin, aldehydes and ammonium acetate for the synthesis of 2,4,5-triaryl-1*H*-imidazoles by using variety of different catalyst like $Yb(OTf)_3$[9], AcOH[10], iodine[11], acidic Al_2O_3[12], silica gel, sodium bisulfate[13], $NiCl_2.6H_2O$[14], NH_4OAc[15], ionic liquid[16] and PEG-400[17].

Hence here we are interested to synthesized 2,4,5-triaryl-1*H*-imidazoles using SnO_2/SiO_2 which is a mesoporous silica supported heterogeneous catalyst with large surface area, high thermal stability and having large range of tunable pores. As it is a nano-composite material show enhanced properties than those of the individual components used separately[18-22].

MATERIALS AND METHODS

General preparation of SnO_2/SiO_2 20 wt % catalyst

The SnO_2/SiO_2 nanocomposite heterogeneous catalyst was prepared by reported method. As reported we have synthesized range of SnO_2/SiO_2 catalyst by using 1.12 gm of tin (IV) chloride which was further dissolved in 25 mL distillated water to that a drop wise tetraethyl orthosilicate solution (3.21 gm) was added after that again cetyltrimethylammonium bromide 1% solution in 25 mL EtOH was added drop wise. The mixture was kept in autoclavable for 11 hrs at 60 °C then the mixture was dried for 6 hrs in oven at 120 °C the dried mixture was powdered by using mortar and pestle. After that the powder was calcined at 350 °C for 3 hrs. Further 10,15 and 25 wt % SnO_2/SiO_2 catalysts were prepared respectively.

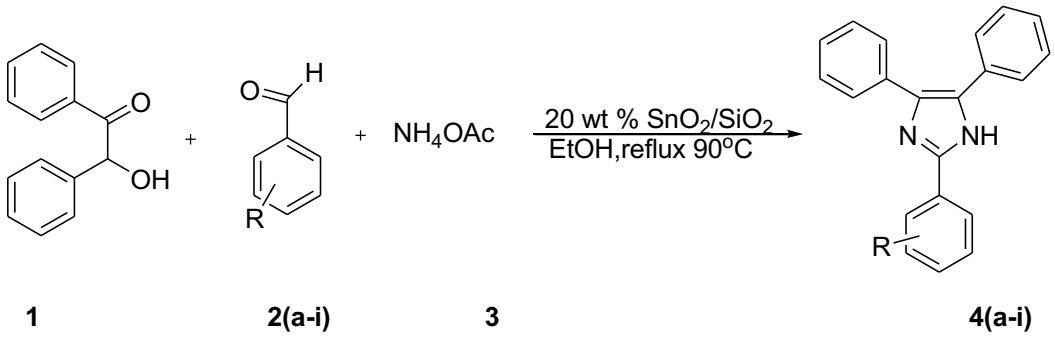
Procedure for the Synthesis of 2,4,5-triaryl-1*H*-imidazoles 4(a-i)

For the synthesis of 2,4,5-triaryl-1*H*-imidazoles a benzoin (**1**) (1.0 mmol) and ammonium acetate (3 mmol) (**3**) mixture was dissolved in RBF (round bottom flask) to that aromatic aldehyde (**2**) (1 mmol) was added and then the catalyst 20 wt % SnO_2/SiO_2 (0.5 g) was added to it and then after the mixture was reflux at 90°C for the respective time as given in **Table 3**.The reaction was monitor by using TLC at regular time interval. After the complete conversion the reaction mixture was poured onto ice and the solid product was separated was filtered and recrystallized using ethanol. And here the catalyst 20 wt % SnO_2/SiO_2 which is not soluble in ethanol, hence easily separated and reused.

Spectral data of some representative compounds

2-(4-Methoxyphenyl)-4,5-diphenyl-1H-imidazole (**4a**)
IR (KBr): 3454 (N_H), 1620 (C-C), 1380 (C-O), 1580 (C-N) cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz;
d, ppm): 3.80 (s, OCH_3), 7.0 (d, 2H, J= 8.8 Hz, Ar), 7.40-7.70 (m, 10H, Ph), 7.80 (d, 2H, J=8.8 Hz, Ar). EIMS (m/z,%): 327 (M^{+1}).
2,4,5-Triphenyl-1H-imidazole (**4c**)
IR (KBr): 3050 (C-H), 3452 (N-H), 1583 (C-N), 1600 (C-C) cm^{-1}.^1H NMR ($CDCl_3$, 80 MHz; d, ppm): 7.20-8.2 (m, 15H, Ph), 9.30 (br s, NH). EIMS (m/z,%): 297 (M^{+1}).
2-(4-Nitrophenyl)-4,5-diphenyl-1H-imidazole (**4e**)
IR (KBr): 3430 (N-H), 1570 (C-N), 1340 (NO_2), 1510 (NO_2), cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz; d, ppm): 7.20-7.80 (m, 10H, Ph), 7.80-8.30 (AB, 4H, J=0.9 Hz, Ar). EIMS (m/z,%): 342 (M^{+1}).
2-(4-Chlorophenyl)-4,5-diphenyl-1H-imidazole (**4h**)

IR (KBr): 1584 (C-N), 3452 (N-H), 1600 (C-C) cm^{-1}. ^1H NMR ($CDCl_3$, 80 MHz; d, ppm): 7.20-7.60 (m, 10H, Ph), 7.40 (d, 2H, J=10 Hz, Ar), 7.80 (d, 2H, J=10 Hz, Ar). EIMS (m/z,%): 331 (M^{+1}).



1 **2(a-i)** **3** **4(a-i)**

Scheme: Synthesis of 2,4,5-triarylimidazoles catalyzed by 20 wt % SnO_2/SiO_2 using ethanol as solvent.

Table 1: Effect of solvents on the synthesis of 2,4,5-triaryl-1*H*-imidazoles

Entry	Solvent	Time (min)	Yield %
1	THF	180	45
2	DMSO	185	40
3	CH_2Cl_2	165	40
4	CH_3CN	150	50
5	Dioxane	145	53
6	Toluene	140	50
7	MeOH	110	76
8	**EtOH**	**70**	**90**
9	H_2O	120	73
10	1:1 EtOH:H_2O	130	68

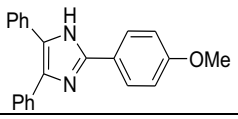
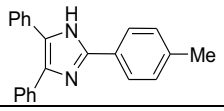
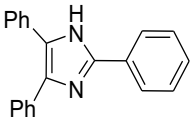
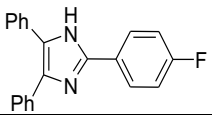
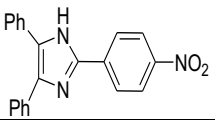
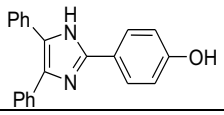
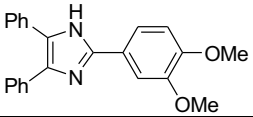
[a]Reaction condition: benzoin (**1**) (1.0 mmol), benzaldehyde (**2**) (1.0 mmol), ammonium acetate (3.0 mmol) and 20 wt % SnO_2/SiO_2 (0.5g) catalyst and reflux.
[b]Isolated yields.

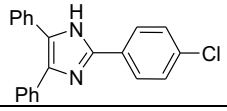
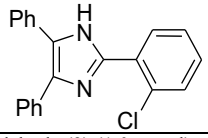
Table 2: Effect of amount of catalyst

Entry	Catalyst	Time (min)	Yield %
5a	-	300	-
5b	SiO_2	160	30
5c	SnO_2	120	44
5d	10 wt % SnO_2/SiO_2	90	60
5e	15 wt % SnO_2/SiO_2	80	76
5f	**20 wt % SnO_2/SiO_2**	**70**	**94**
5g	25 wt % SnO_2/SiO_2	70	85

[a]Reaction condition: benzoin (**1**) (1.0 mmol), benzaldehyde (**2**) (1.0 mmol), ammonium acetate (3.0 mmol) and EtOH as solvent and reflux.
[b]Isolated yields.

Table 3: Synthesis of 2,4,5-triaryl-1*H*-imidazoles using catalyst 20 wt % SnO_2/SiO_2

Entry	Aldehyde (R)	Time (min)	Product	M.P (°C)	Yield (%)
4a	4-OMe	60		228 -230	97
4b	4-Me	75		231-233	95
4c	H	80		276-278	90
4d	4-F	75		188-190	90
4e	4-NO_2	95		232-233	88
4f	4-OH	70		269-270	94
4g	3,4-(OMe)	55		221-223	95

4h	4-Cl	75		260-262	93
4i	2-Cl	85		195-197	86
[a]Reaction condition: benzoin (**1**) (1.0 mmol) ,benzaldehyde (**2**) (1.0 mmol), ammonium acetate (3.0 mmol) and 20 wt % SnO_2/SiO_2 (0.5g) catalyst and reflux at 90°C for 70 min. [b]Isolated yields.					

RESULT AND DISCUSSION

The present scheme involves a synthesis of 2,4,5-triaryl-1H-imidazoles (**4a-i**) by the condensation of Bezoin (**1**), with aromatic aldehydes (**2a -i**) and ammonium acetate (**3**) in the presence of 20 wt % SnO_2/SiO_2 as catalyst and ethanol as solvent and was reflux at 90°C. Here we have observed that for all the different aldehydes we have used we got good yields as given in (**Table 4**).

Effect of solvent: Screening of different solvents from non-polar to polar as THF, DMSO, CH_2Cl_2, CH_3CN, Dioxane, Toluene, CH_3OH, C_2H_5OH, H_2O, 1:1 EtOH : H_2O. Here we have observed that the excellent conversion take place in less time by the use of EtOH (entry 8, **Table 1**). Also many others (entries 7,9,10, **Table 1**) shows good yields but takes more time for conversion.

Effect of catalyst amount: To know proper composition and activity of catalyst we have carried out the reaction with different composition, where we observed that without catalyst the desired product was not formed and when SiO_2 and SnO_2 where used separately gave poor yields but when SiO_2 and SnO_2 where used in mixture gave good yield. Then after to confirm the optimum amount of catalyst required for the reaction, we have performed the reaction with different percentage of catalyst and it was observed that the catalyst with 20 wt % SnO_2/SiO_2 (entry 5f, **Table 2**) gave excellent yield. Here we have recycled catalyst simply by filtration and was washed with n-hexane and dried at 90°C and the catalyst was used for next run. In way the catalyst was recycled and reused used for two to three times.

CONCLUSION

In conclusion, we report a efficient method for the synthesis 2,4,5-triaryl-1H-imidazoles where we have used a heterogeneous nanocomposite catalyst SnO_2/SiO_2 which is easily recycled and reused. And also use of ethanol as solvent, which makes this method more efficient and green. Further studies and application of this methodology for the synthesis of other interesting heterocycles are underway in our laboratory.

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