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Microwave assisted sulphamic acid catalysed one pot synthesis of 2, 4, 5 triaryl-1*H*-imidazoles via. Condensation reaction

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ABSTRACT

A simple and high yielding one pot method for synthesis of 2, 4, 5 triaryl imidazoles from condensation of benzil, ammonium acetate and aromatic aldehydes using sulphamic acid (H_2NSO_3H) catalyst is described. The short reaction time (95 to 130 sec.), cleaner reaction and easy work up make this protocol practically and economically attractive.

KEYWORDS

Benzil;
Ammonium acetate;
Aromatic aldehyde;
Sulphamic acid;
Triaryl imidazoles.

INTRODUCTION

Triaryl imidazole compounds have gained remarkable importance due to their widespread biological activities and their use in synthetic chemistry. The imidazole ring system is one of the most important substructure found in a large number of natural products and pharmacologically active compounds. For example, the amino acid histidine, the hypnotic agent etomidate[1], the antiulcer-active agent cimetidine[2], the proton pump inhibitor omeprazole[3], the fungicide ketoconazole[4], and the benzodiazepine antagonist flumazenil[5] are imidazole derivatives. In recent years, substituted imidazoles are substantially used in ionic liquid[6], that has given a new approach to 'Green Chemistry'. In addition, they are used in photography as photosensitive compound[7]. Literature survey reveals several methods for synthesizing them, mainly using nitriles and esters[8-10] as the starting substrates. Japp and Radziszewski proposed the first synthesis of the imidazole core in 1882, starting from 1, 2, dicarbonyl compounds aldehydes and ammonia to obtain 2, 4, 5 triphenylimidazoles[11, 12]. Subsequently, many other syntheses of this important heterocycle have been published[13]. For example, 2, 4 – diaryl -1*H*- imidazoles are often obtained from amidines and R-bromo arylketones[14].

The number of methods have been developed for the synthesis of 2, 4, 5 trisubstituted imidazoles. The 2, 4, 5 trisubstituted imidazoles are generally synthesized by three-component cyclocondensation of a 1,2-diketone, α-hydroxyketone or α-ketomonoxime with an aldehyde and ammonium acetate, which comprise the use of ionic liquids[15], refluxin in acetic acid[16], silica sulfuric acid[17], $NiCl_2.6H_2O/Al_2O_3$[18], $Yb(OTf)_3$[19], $Yb(OPf)_3$[20], iodine[21], $Zr(acac)_4$[22], $InCl_3.3H_2O$[23], heteropolyacid[24], sodium bisulfite[25], potassium aluminum sulfate (alum)[26], ceric ammonium nitrate (CAN)[27], polymer-supported $ZnCl_2$[28] and L-proline[29].

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Sulphamic acid has been emerged as a promising solid acid catalyst for acid catalyzed reactions, such as functional group protections and deprotections and the synthesis of isoamyl acetate and polymeric ethers. Moreover, some important organic transformations, including the Beckmann rearrangement and Biginelli condensations[30], have been performed successfully in the presence of sulphamic acid.

EXPERIMENTAL

The melting point was taken in open capillaries in Paraffin bath and is uncorrected. IR spectra were recorded in KBr disc on a Perkin Elmer spectrometer for all products ^{1}H-NMR spectra were recorded on NMR spectrometer in $CDCl_3$ using chloroform as an internal standard. The mass spectra were recorded on GCMS-QP 2010 mass spectrometer. All the reagents used were of AR grade and were used without further purification. The reactions were carried out in microwave oven (CE2977 Samsung).

All compounds were characterized by modern spectral and elemental techniques.

1a: 2, 4, 5 triaryl – 1H – imidazole (off white solid M. P. 277-278°C).

IR (KBr): 3061 (N - H), 1595 (C=C), 1488 (C=N), ^{1}H NMR (400Mz, $CDCl_3$): δ = 7.25 – 7.97 (m, 15 H Ar - H), 8.15 (brs, NH), ES-MS: m/z = 296 [M - H].

Anal. Cald for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45 Found: C, 85.24; H, 5.62; N, 9.47

1b: 2(4 - Chlorophenyl) – 4, 5 – diphenyl – 1H – imidazole (off white solid M. P. 260-261°C).

IR (KBr): 3452 (N - H), 1620 (C=C), 1580 (C=N), ^{1}H NMR (400Mz, $CDCl_3$): δ = 7.10 – 7.60 (m, 15 H Ar - H), 7.35 (d, 2H, Ar), 7.85 (d, 2H Ar), 9.30 (brs, NH), ES-MS m/z = 330 [M - H].

Anal. Cald for $C_{21}H_{15}ClN_2$: C, 76.24; H, 4.57; N, 8.47 Found: C, 76.28; H, 4.59; N, 8.48

1c: 2(2 - Chlorophenyl) – 4, 5 – diphenyl – 1H – imidazole (off white solid M. P. 196-197°C).

IR (KBr): 3070 (N - H), 1580 (C=C), 1490 (C=N), ^{1}H NMR (400Mz, $CDCl_3$): δ = 7.5 – 7.65 (m, 6 H), 7.68 -7.72(m, 2H), 7.9 – 8.0 (m, 6H), (brs, 1H), ES-MS: m/z = 330 [M - H].

Anal. Cald for $C_{21}H_{15}ClN_2$: C, 76.24; H, 4.57; N, 8.47 Found: C, 76.26; H, 4.59; N, 8.48

1f: 2(4 - hydroxyphenyl) – 4, 5 – diphenyl – 1*H* – imidazole (off white solid M. P. 267-268°C).

IR (KBr): 3220 (N - H), 1615 (C=C), 1582 (C=N), ^{1}H NMR (400Mz, $CDCl_3$): δ = 6.70 – 7.61 (m, 15 H Ar - H), 9.52 (brs, NH), ES-MS : m/z = 312 [M - H]

Anal. Cald for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97 Found: C, 80.78; H, 5.20; N, 8.99

RESULTS AND DISCUSSION

TABLE 1 : Physical data of the synthesized compounds

Compd	Aldehyde	Watt	Time	Yield	M.P./ B.P.(°C)	
		W	Sec.	%	Found	Reported
Ia	Benzaldehyde	600	105	96	277-278	276-277[10]
Ib	4 –Cl – Benzaldehyde	600	110	94	260-261	261-263[25]
Ic	2-Cl-Benzadehyde	600	95	94	196-197	197-198[25]
Id	4-$N(CH_3)_2$-Benzadehyde	600	98	92	256-257	257-258[10]
Ie	4-NO_2-Benzaldehyde	600	112	91	235-236	236-238[25]
If	4-OH-Benzaldehyde	600	115	93	267-268	268-269[25]
Ig	3,4-$(OCH_3)_2$-Benzadehyde	600	105	94	218-219	216-218[10]
Ih	4-OCH_3-Benzaldehyde	600	120	92	227-228	227-228[10]
Ii	4-CH_3-Benzaldehyde	600	118	94	230-231	231-232[10]
Ij	4-Br-Benzaldehyde	600	130	94	263-265	261-263[25]
Ik	2-Furan	600	110	96	201-202	202-203[31]

In order to find optimum reaction conditions, condensation of Benzil, Benzaldehyde and ammonium acetate in the presence of sulphamic acid as catalyst was done. The optimum molar ratio of Benzil: benzaldehyde: ammonium acetate 1:2:1 and sulphamic acid (2 mol%) using ethanol solvent under microwave irradiation, 2(phenyl) 4, 5 – diphenyl 1H – imidazole was obtained with 96% yield at 600 Watt for 105 sec. Results with benzaldehydes were encouraging, in a similar fashion, a

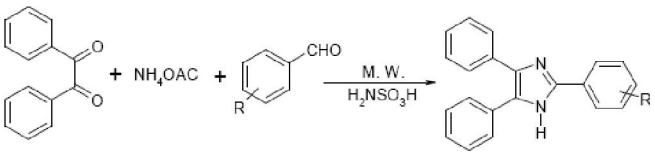
variety of aromatic and heterocyclic aldehyde and benzil subjected to this novel procedure gives high yields of corresponding 2, 4, 5, triaryl imidazole.

The results are summarized in TABLE - 1. From the results mentioned in TABLE the aldehyde with electron-donating substituents favor the reaction and it was completed with shorter reaction time and high yields than the aldehyde with electron-withdrawing substituents. Also, the present method was found to be effective for hetero-aromatic aldehyde for the synthesis of 2- heteroaryl 4, 5 diphenyl 1H imidazole with better yield. To determine the role of sulphamic acid, the same reaction was carried out in the absence of catalyst at same conditions, which resulted in no product formation after 15 min.

These results indicate that sulphamic acid exhibits a high catalytic activity in this transformation. The procedure gives high yield products.

Comparison of results as mentioned in TABLE -1 with results obtained by some other reported procedures for synthesis of 2, 4, 5 triaryl imidazoles shows the promising feature of this method in terms of reaction rate and the yield of products as compared with reports in the literature.

REACTION



CONCLUSION

In conclusion, we have developed a simple, efficient and clean methodology for synthesis of 2, 4, 5 triaryl imidazole derivatives by condensation of benzil, substituted aromatic aldehydes and ammonium acetate in the presence of sulphamic acid (NH_2SO_3H) catalyst at 600 Watt for 95 to 130 sec. and get the condensed products in superior yields. In this procedure the ethanol is used as solvent and therefore it is relatively ecofriendly. The notable merits of this method are short reaction time, simple work up procedure, superior yield of products, nontoxic, nonvolatile and noncorrosive acid catalyst which makes this method a valid contribution to the existing methodologies.

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