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EFFICIENT SYNTHESIS AND CHARACTERISATION OF IMIDAZOLES UNDER MICROWAVE IRRADIATION

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ABSTRACT

A simple and highly efficient imidazoles have been synthesized in a very good yield under microwave irradiation by reaction of 2- bromo-1- (substituted phenyl) ethanone with substituted amides such as urea, thiourea, guanidine using ethanol as a solvent in the presence of triethyl benzyl ammonium chloride (TEBA) as a phase transfer catalyst.The short reaction time, cleaner reaction, and easyworkup make this protocol practical and economically attractive.

Keywords: TEBA catalyst, 2- bromo-1- (substituted phenyl) ethanone, substituted amide, microwaveirradiation.

INTRODUCTION

To design and conduct chemical reactions with "green" experimental protocol is an enormouschallenge that chemists have to confront to improve the quality of the environment for presentand future generations. Target areas for achieving this goal are the exploration of alternativereaction conditions and reaction media to accomplish the desired chemical transformations withminimized by-products or waste,Over the past several years, chemists have been aware of the environmental implications of their chemistry. Nowadays, they are trying to develop new synthetic methods, reaction conditions, and uses of chemicals that reduce risks to humans and the environment.Imidazole was first reported by Debus[1] in 1858, fully developed by Radziszewskibeginning in 1882, and further modified by Weidenhagen in 1935. It is the synthesis of an imidazole derivative by the condensation of and α-dicarbonyl compound (e.g. glyoxal), an aldehyde and two equivalents of dry ammonia in alcohol. Therefore, this reaction is generally known as Radziszewski reaction, occasionally called as Radziszewski synthesis, Weidenhagen synthesis or Debus- Radziszewski imidazole synthesis.Compounds with an imidazole ring system have many pharmacological properties and play important role in biochemical processes.[2] Many of the substituted imidazoles are known asinhibitors of fungicides and herbicides, plant growth regulators and therapeutic agents.[3] Recentadvances in green chemistry and organometallic chemistry have extended the boundary ofimidazoles to the synthesis and application of a large class of imidazoles as ionic liquids andimidazole related N-heterocyclic carbenes.[4]

There are several methods reported in the literature for the synthesis of imidazoles such as Thehetero-Cope rearrangement,[5]four-component condensation of arylglyoxals, primary amines,carboxylic acids and isocyanides on Wang resin,[6] reaction of N-(2-oxo)-amides with ammoniumtrifluoroacetate, 1,2-aminoalcohols in the presence of PCl5, diketones, aldehyde, amine andammonium . Several microwave (MW) assisted syntheses of imidazoles from 1,2-diketones and aldehydes in the presence of a variety of catalysts such as silica-gel, silica-gel/HY,Al2O3, DMF, acetic acid,[7]ZrCl,[8] $NiCl_2.2H_2O$,[9]and ionic liquid,[10] also by using thiourea[11,12].

The use of microwave for the synthesis of organic compounds proved to be efficient, safe, and environmentally benign technique, with shorter reaction time,high yields and easier manipulation.

EXPERIMENTAL

All the synthesized compounds have been characterized on the basis of chemical properties, elemental and spectral analysis. The melting points were measured in a open glass capillary and are uncorrected. IR spectra in KBr were recorded on instrument Shimadzu FT-IR. ^{1}H-NMR spectra were recorded on varian mercury YH-300, 400 MHz ($CDCl_3$ and DMSO-d_6) spectrophotometer using TMS as an internal standard. All reactions were monitored by TLC using silica gel 60-f 254 plates. The reactions were carried out in scientific microwave oven (scientific microwave system model RG31L1, 700w, 2450 MHz). Satisfactory C, H, N analyses were carried out for most of the compounds on Perkin-Elmer 2400 CHN analyzer at RSIC, Punjab University, Chandigarh.

General procedure for the synthesis of 4-(substituted phenyl)-1H-imidazol-2(5H)-one/thione/ imine

2-Bromo-1-(substituted phenyl) ethanone**(IIa-c)** (0.02 M) dissolved in ethanol and substituted amide/imidine (0.02 M) in water using TEBA (0.05 M) as catalyst were irradiated under microwave for 3.5 min at 700 W. The reaction mixture was allowed to cool and triturate it. Add ice-cold water and neutralize with sodium acetate. The product thus separated out was filtered and crystallized from ethanol as 4-(substituted phenyl)-1H-imidazol-2(5H)-one/thione/imine **(IIIa-i)** in 60 to 80% yield. The products were confirmed by IR and ^{1}H NMR spectra and melting point.

Spectral data of principal compound

Synthesis of 4-(2'-hydroxy-5'-methylphenyl)-1H-imidazol-2(5H)-thione (IIIb)

IR (KBr) : 3172 (vb,OH), 3032 (s,-C-H), 1631(s,-C=C), 1481(s, –C=N), 1006 (s,-C-N) cm^{-1}. ^{1}H NMR $CDCl_3$,300 MHz , δ, ppm): 2.1(s,3H, -CH_3) 2.3 (s,1H, NH),4.2 (s, 2H, -CH_2) 7.4 - 7.7(m, 3H, Ar-H) 12.1(s, 1H,-OH)

Synthesis of 4-(4'-chloro phenyl)-1H-imidazol-2(5H)-one (IIId)

IR (KBr) : 3369(s,NH),3170 (s,-C-C), 1697(s,-C=O), 1487(s, –C=N), 1010 (s,-C-N), 777 (s,-C-Cl) cm^{-1}. ^{1}H NMR $CDCl_3$,300 MHz , δ, ppm): 0.91(s,1H, NHtautomeric) 1.2(s,1H, NH), 4.3 (s, 2H, -CH_2) 4.6(s,1H,=CH tautomeric) 7.3 (d,J=9Hz, 2H, Ar-H) 7.9(d,J=9Hz, 2H, Ar-H)

Synthesis of 4-(4'-chloro phenyl)-1H-imidazol-2(5H)-imine (IIIf)

IR (KBr) :3360 (s,-NHstreach), 1697 (s,-C=C), 1485(s,-C=N), 1093(s, –C- N), 817 (s,-C-Cl)559(s,-C=C-N) cm^{-1}. ^{1}H NMR $CDCl_3$,300 MHz , δ, ppm): 1.50(s, 1H,-NHtautomeric) 1.60(s,1H,-NH) 3.50(s,1H=NHtautomeric) 4.66(s,2H, -CH_2) 7.75(d,J=9Hz, 2H, Ar-H) 7.91(d,J=9Hz, 2H, Ar-H)

RESULTS AND DISCUSSION

In order to find optimum reaction conditions 2-Bromo-1-(2'-hydroxy-5'-methyl phenyl) ethanone(IIb) (0.02 M) dissolved in ethanol and thiourea (0.02 M) in water using TEBA (0.05 M) as a catalyst were irradiated under microwave for 3.5 min at 700 W. The reaction mixture was allowed to cool, poured in ice-cold water and neutralize it with sodium acetate. The product thus separated out was filtered and crystallized from ethanol as fine crystal to get 4-(2'-hydroxy-5'-methylphenyl)-1H-imidazol-2(5H)-thione(IIIb)

in 78% yield.we were encouraged by the results obtained for 4-(2'-hydroxy-5'-methylphenyl)-1H-imidazol-2(5H)-thione(IIIb)In asimilar fashion we get result forSynthesis of 4-(4'-chloro phenyl)-1H-imidazol-2(5H)-one (IIId) in 70% yield.

Synthesis of 4-(4'-chloro phenyl)-1H-imidazol-2(5H)-imine (IIIf) in 68 % yield.

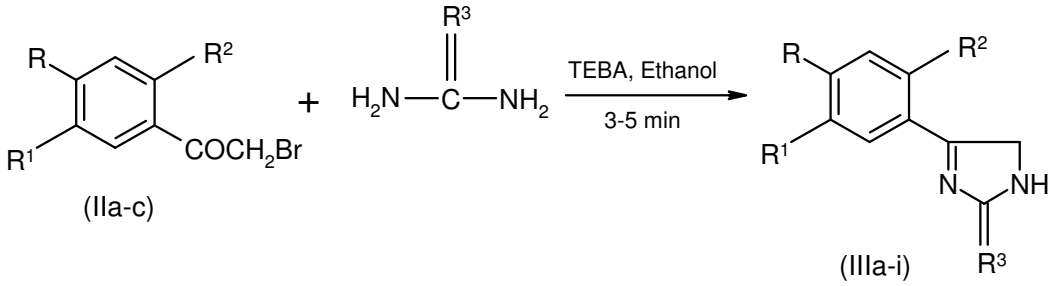
In the table 1, we have compared result with result obtained by conventional method for the synthesis of 4-(substituted phenyl)-1H-imidazol-2(5H)-one/thione/imine (IIIa-i)with microwave irradiation synthesis.

CONCLUSION

In conclusion we have investigated that benzyl triethyl ammonium chloride work as an excellent catalyst and reactions carried in microwave irradiation gives more yield as compared to conventional method. The notable merit offered by this method are : the catalyst is inexpensive and readily available , simple procedure, reaction time is short, with high yields and the reaction conditions are environment friendly.

Table-1: Synthesis of 4-(substituted phenyl)-1H-imidazol-2(5H)-one/thione/imine

Expt. No.	α-halocarbonyl compound	4-(substituted phenyl)-1H-imidazol-2(5H)-one/thione/imine	m.p. (°C)	M.F.	M.W. Yield (%)	Conv. Yield (%)
1	2-Bromo-1-(2-hydroxy-5-methyl phenyl) ethanone (IIa)	4-(2-Hydroxy-5-methyl phenyl)-1H-imidazol-2(5H)-one (IIIa)	96	$C_{10}H_{10}N_2O_2$	78	50
2	(IIa)	4-(2-Hydroxy-5-methyl phenyl)-1H-imidazol-2(5H)-thione (IIIb)	50	$C_{10}H_{10}N_2OS$	60	55
3	(IIa)	4-(2-Hydroxy-5-methyl phenyl)-1H-imidazol-2(5H)-imine (IIIc)	100	$C_{10}H_{11}N_3O$	65	40
4	2-Bromo-1-(4-chloro phenyl) ethanone (IIb)	4-(4-chlorophenyl)-1H-imidazol-2(5H)-one (IIId)	90	$C_9H_7ClN_2O$	70	60
5	(IIb)	4-(4-chlorophenyl)-1H-imidazol-2(5H)-thione (IIIe)	110	$C_9H_7ClN_2OS$	75	55
6	(IIb)	4-(4-chlorophenyl)-1H-imidazol-2(5H)-imine (IIIf)	160	$C_9H_8ClN_3$	68	50
7	2-Bromo-1-(4-nitro phenyl) ethanone (IIc)	4-(4-nitrophenyl)-1H-imidazol-2(5H)-one (IIIg)	132	$C_9H_7N_3O_3$	78	65
8	(IIc)	4-(4-nitrophenyl)-1H-imidazol-2(5H)-thione (IIIh)	98	$C_9H_7N_3O_2S$	63	50
9	(IIc)	4-(4-nitrophenyl)-1H-imidazol-2(5H)-imine (IIIi)	48	$C_9H_8N_4O_2$	75	55



Compound	R	R^1	R^2	R^3
IIIa	H	CH_3	OH	O
IIIb	H	CH_3	OH	S
IIIc	H	CH_3	OH	NH
IIId	Cl	H	H	O
IIIe	Cl	H	H	S
IIIf	Cl	H	H	NH
IIIg	NO_2	H	H	O
IIIh	NO_2	H	H	S
IIIi	NO_2	H	H	NH

Scheme-1: Synthesis of 4-(substituted phenyl)-1H-imidazol-2(5H)-one/thione/imine (IIIa-i) from 2-Bromo-1-(substituted phenyl) ethanone(IIa-c) and substituted amide.

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