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Synthesis and Characterization of Benzimidazole by Using o-Phenylenediamine with Different Aldehydes and Carboxylic Acids in the Presence of ρ-T_sOH as a Catalyst

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ABSTRACT

This research paper deals with the synthesis and diagnose of Benzimidazole rings which were have been prepared by using two different methods in which used starting material o-phenylenediamine with different compounds. The first method is with aldehydes such as 4-Chlorobenzaldehyde, 4-N, N-Dimethylbenzaldehyde, and Formaldehyde. The second is with carboxylic acids such as salicylic acid, acetic acid, and butanoic acid. ρ-T_sOH has been using as a catalyst in the synthesis methods above and used F.T.I.R and HNMR spectroscopy are used for diagnosing the prepared rings in addition to the physical properties.

Keywords: Aldehydes, Benzimidazole, Carboxylic Acids, ρ-(Tolune sulphonic acid).

INTRODUCTION

Benzimidazole is one of the heterocyclic compounds that shows different biological qualities such as antibacterial and antifungal[1]. Also, some Benzimidazoles have an effect on human viruses such as cytomegalovirus[2]. There are two procedures for the synthesis of 2-substituted Benzimidazoles. The first is the reaction of phenylenediamines and carboxylic acids or its derivatives by heating[3] in strong drying conditions[4]. The second includes a two-step procedure that includes the oxidative cyclodehydrogenation of Schiff bases, which are often generated from the condensation of phenylenediamines and aldehydes[3] and with aryl-aldehydes by using an acidic agent and also with silica gel at room temperature[4]. ρ-TsOH has been used as a neutral acid catalyst to synthesize a number of benzimidazoles[5]. It is considered as an important, effective, available and inexpensive incentive[6]. Also, there are many ways to synthesize benzimidazole by using different catalysts such as Nanocrystalline oxides with iodine[7], H_2O_2/HCl and $Cu(OTf)_2$[8], HCl[9]. In this work, the aim was the synthesis of benzimidazole rings by using one catalyst is ρ-TsOH as in previous studies above, which have used one catalyst in different circumstances.

Instruments

1- Melting points have been determined by using Melting pointSMP3 apparatus.
2- F.T.I.R spectra have been recorded by using Fourier Transform Infrared Spectrophotometre (F.T.I.R) 8400 S Shimadzu apparatus.
3- HNMR spectra have been recorded by using NMR Spectrometer 400 MHz, Avance III 400 Bruker, Germany.
4- U.V. spectra have been recorded by using U.V-Visible Spectrophotometer 1650 PC Shimadzu apparatus.

EXPERIMENTAL

The General Method for Synthesizing Benzimidazoles from Aldehydes

A solution of Aldehyde (0.01 mole), o-phenylenediamine(0.01 mol) and DMF (3 ml) has been mixed with ρ-TsOH (20 ml). The mixture has been heated and stirred at 80C° for 2-3 h then cooled to reach room temperature, the mixture has been added dropwise with stirring into mixture of Na_2CO_3 (0, 01mole) and H_2O (20 ml), the product has been filtered, washed by H_2O, then dried[2] to yield A, B and C compounds.

The General Method for Synthesizing Benzimidazole from Carboxylic Acids

A solution of Carboxylic acid (0.01 mole), o-phenylenediamine(0.01 mole) and toluene (10 ml) has been mixed with ρ-TsOH (20 ml). The mixture has been refluxed for 2-3 h then cooled, filtered and dried[10] to yield D, E and F compounds.

RESULT AND DISCUSSION

Synthesis compounds characterized by F.T.I.R. and H-NMR spectroscopy have showed an important absorption packs of functional groups for the synthesis Benzimidazole derivatives from aldehydes and carboxylic acids with presence of ρ-T_SOH as a catalyst in the different conditions.

2-(4-Chlorophenyl) -1*H*-Benzimidazole (A)

The F.T.I.R spectrum of this compound shows appearance of an absorption pack at 3379 cm^{-1} refers to (N-H) group and appearance of an absorption pack at 686 cm^{-1} refers to (C-Cl) bond. HNMR (400 MHz) δ(ppm) Benzi. (7.26t 2H) and (7.71t 2H), Ar (7.31 and 7.61), N-H(3.42s). Table (2) shows the other absorption packs of the compound in the F.T.I.R spectrum.

2-(4-N,N- Dimethylaniline)-1*H*-Benzimidazole (B)

The F.T.I.R spectrum of this compound shows an absorption pack at 3301 cm^{-1} refers to (N-H) group and appearance of an absorption pack at 2916 cm^{-1} refers to (C-H) aliphatic. H-NMR (400 MHz) δ(ppm) Ar (6.91 and 7.31), Benzi. (7, 26t 2H 7.69t 2H), N-H(4.42d), CH_3(2.91). Table (2) shows the other absorption packs of the compound in the F.T.I.R spectrum.

1H-Benzimidazole (C)

The F.T.I.R spectrum of this compound shows an absorption pack at 3409 cm^{-1} refers to (N-H) group and an absorption pack at 2923 cm^{-1} refers to (C-H) aliphatic. HNMR (400 MHz) δ(ppm) Benzi. (7.68t 2H) and (7.26-7.30t 2H), N-H(2.9Hz), Benz.-CH(7.90Hz). Table (2) shows the other absorption packs of the compound in the F.T.I.R spectrum.

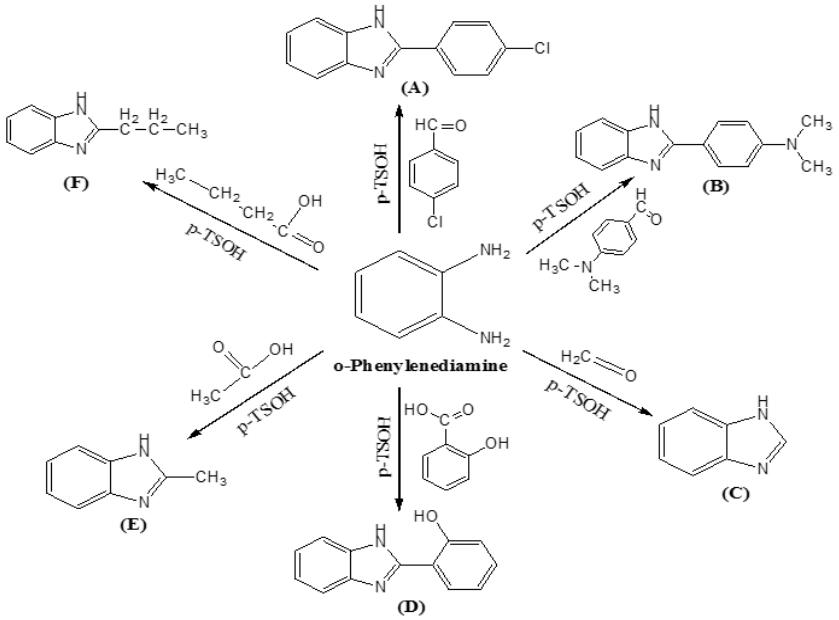
2-(2-hydroxy phenyl)-1H-Benzimidazole (D)

F.T.I.R spectrum of this compound shows an absorption pack at 3425 cm^{-1} refers to (O-H) group

Table 1: Physical Properties of Compounds

Compounds	Molecular formula	Solvent	Yield %	m. p. C°	Color
A	$C_{13}H_9N_2Cl$	DMF	78	294-298	Brown
B	$C_{15}H_{15}N_3$	DMF	72	237-240	Nutty
C	$C_6H_6N_2$	DMF	85	115-118	Yellow
D	$C_{13}H_{10}N_2O$	Toluene	81	151-157	Yellow
E	$C_8H_8N_2$	Toluene	72	Oil	Nutty
F	$C_{10}H_{12}N_2$	Toluene	68	249 dec.	Nutty

and appearance of an absorption pack at 1157 cm^{-1} refers to (C-O) bond in addition to an absorption pack (N-H) group at 3240 cm^{-1}. HNMR (400 MHz) δ(ppm) Benz. (7.26t 2H) and (7.75t 2H), Ar (7.35-7.00), N-H(2,93s), O-H(7.97). Table (2) shows the other absorption packs of compound in F.T.I.R spectrum.



Scheme 1

2-Methyl-1H-Benzimidazole (E)

The F.T.I.R spectrum of this compound shows an absorption pack at 3178 cm^{-1} refers to (N-H) group and an absorption pack at 2916 cm^{-1} refers to (C-H) aliphatic. HNMR (400 MHz) δ(ppm) Benz. (7.26t 2H and 7.71t 2H), N-H(2.45), CH_3 (2.20s). Table (2) shows the other absorption packs of the compound in the F.T.I.R spectrum.

2-Propyl-1H-Benzimidazole (F)

The F.T.I.R spectrum of this compound shows an absorption pack at 3209 cm^{-1} refers to (N-H) group and an absorption pack at 2962 and 2931 cm^{-1} to (C-H) aliphatic. HNMR (400 MHz) δ(ppm) Benz. (7.29t 2H) and (7.71t 2H), N-H(4.28s), $-CH_2-CH_2$(2.42S), CH_2-CH_2-(1,43S), CH_3(0.92S). Table (2) shows the other absorption packs of the compound in the F.T.I.R spectrum.

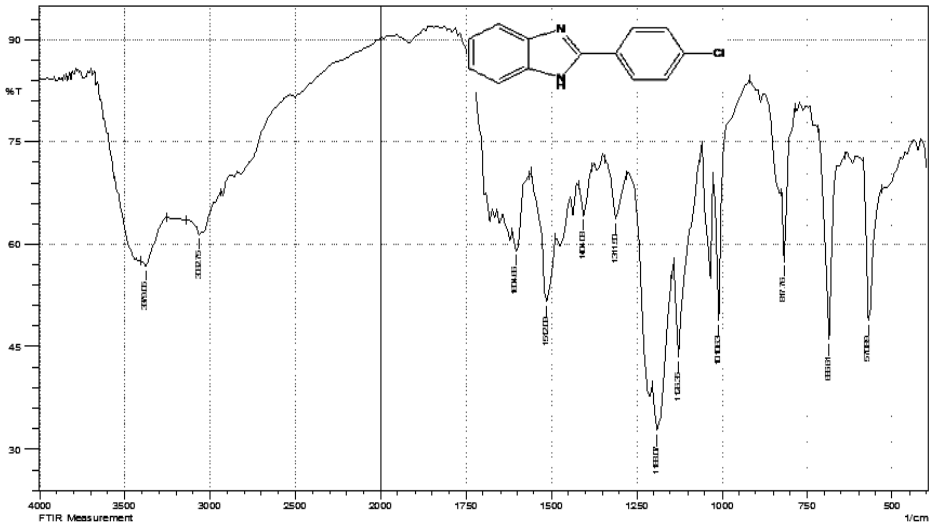


Fig. 1. (F.T.I.R) Spectrum of Compound(A)

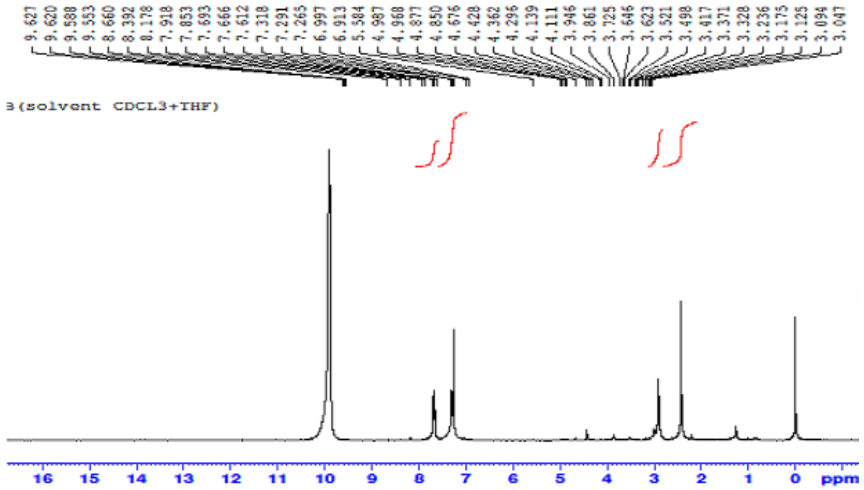


Fig. 2. (H-NMR) Spectrum of Compound(B)

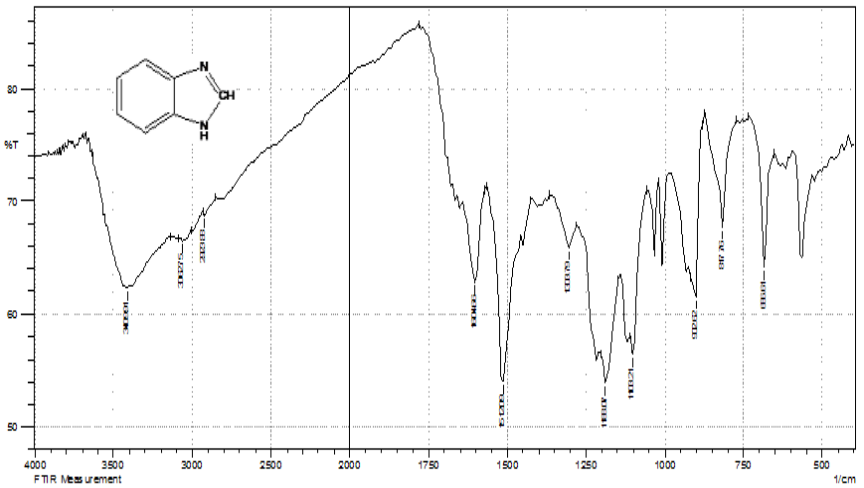


Fig. 3. (F.T.I.R) Spectrum of Compound(C)

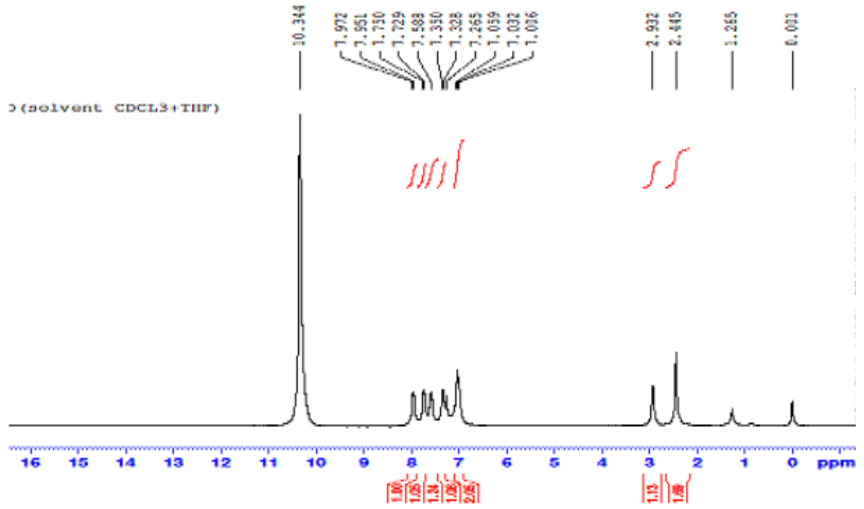


Fig. 4. (F.T.I.R) Spectrum of Compound(D)

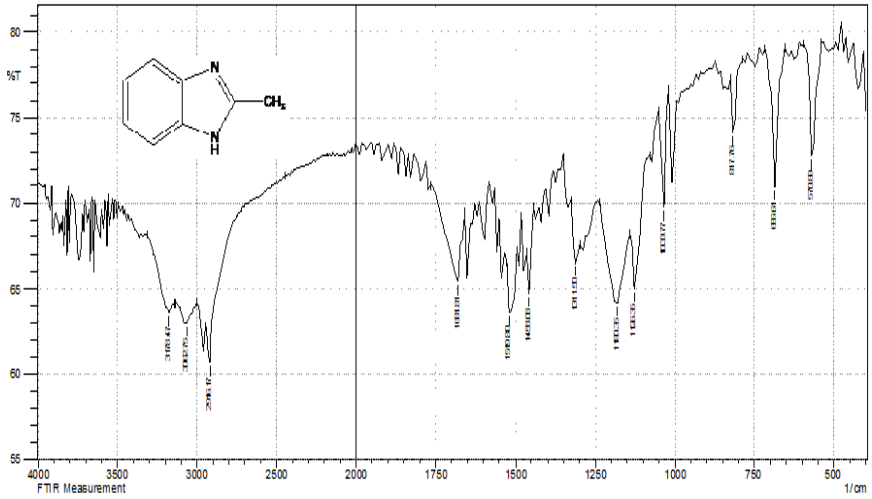


Fig. 5. (F.T.I.R) Spectrum of Compound(E)

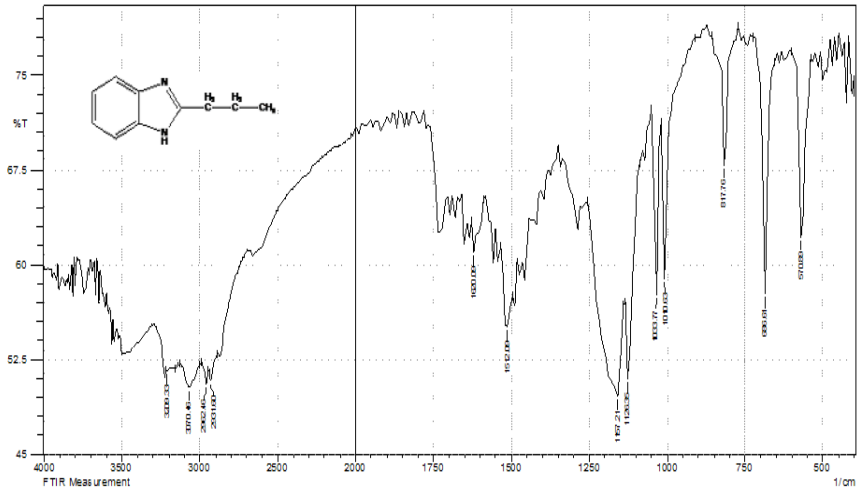


Fig. 6. (F.T.I.R) Spectrum of Compound (F)

Table 2: Absorption Peeks of Compounds in F.T.I.R. Spectroscopy

Compounds	Name of compound	UV (nm)	(C-H) aromatic cm^{-1}	(C=N)(C=C)	(C-N)
A	2-(4-Chlorophenyl) - 1*H*-Benzimidazole	318 379	3062	1512-1604	1311
B	2-(4-N,N- Dimethylaniline) -1*H*-Benzimidazole	293 374	3039	1496-1604	1365
C	1H-Benzimidazle	316	3062	1512-1604	1303
D	2-(2-Hydroxy Phenyl)- 1H-Benzimidazole	293 396	3024	1666-1612	1249
E	2-Methyl-1H-Benzimidazole	357	3062	1519-1681	1311
F	2-Propyl-1H-Benzimidazole	357	3070	1512-1620	1157

CONCLUSION

In this study, a number of rings of benzimidazole have been synthesized from the reaction of o-phenylenediamine with different aldehydes and different carboxylic acids by using ρ-T_SOH as a catalyst in all synthesis processes. The synthesis results have given a high percentage of the products with different solvent used. The spectral techniques FT.I.R and H-NMR have been used to diagnose the prepared rings.

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