Synthesis and Characterization Benzimidazole Ring by Using O-phenylinediamine with Different Compounds and Using Mannich reaction for Preparation of Some Derivatives

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http://dx.doi.org/10.13005/ojc/340152

(Received: July 24, 2017; Accepted: October 02, 2017)

ABSTRACT

The research includes synthesis and characterization Benzimidazole rings by using different compounds such as Urea, Thiourea and Carboxylic acid by reactant with O-phenylinediamine, then substitution hydrogen atom with present on nitrogen atom by reactant with primary and secondary amines according to Mannich reaction. Compounds was organized by using F.T.I.R and HNMR spectroscopy.

Keywords: Benzimidazole, O-phenylinediamine, Thiouria, Amines, Mannich reaction.

INTRODUCTION

Benzimidazole is heterocyclic compound found in many natural and non-natura1 products, such as some vitamins. Therefore, benzimidazole substitutes tooks the attention of different research groups, especially as compensation or replacement in the position 1,2 is very important sites in the impact of drug effective. In this study reported some of the ways to prepare benzimidazole 2-substitution, for the importance of this compound in the field of antibiotics, such as cancer, angiotensin-II receptor antagonest and antimicrobial properties. The NH group compounds are able to entering into N-alkylation and N-acylation according to Mannich and Michael reaction as in isatin compounds, which are similar with benzimidazoles. Mannich reaction very important reaction by converting some of the prepared compounds into other compounds are more important than in the biological field.

MATERIALS AND METHODS

1- Melting points were determined by using Melting PointSMP3 apparatus.
2- F.T.I.R. spectra were recorded by using Fourier Transform Infrared Spectrophotometer
EXPERIMENTAL

Synthesis 1,3-dihydro-benzimidazol-2-substitution (A and B)
A mixture of o-phenylenediamine with urea to yield (A) and with thiourea to yield (B) in existence of HCl in equal concentrations was heated at 130 °C under reflux in alcohol solution until the evolution of ammonia ceased.

Synthesis 2-Phenol-1H-benzimidazol (C)
A mixture of equal concentration (0.01 mol) of o-phenylenediamine and Salicylic acid in 4N HCl (20 ml) was refluxed for 30 min. then cooled, filtered and recrystallized from absolute alcohol.

Table 1: show physical properties of compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Solvent</th>
<th>Yield %</th>
<th>m.p. C</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>C_7H_6N_2O</td>
<td>Ethanol</td>
<td>94</td>
<td>275-279</td>
<td>Yellow</td>
</tr>
<tr>
<td>B</td>
<td>C_7H_6N_2S</td>
<td>Ethanol</td>
<td>66</td>
<td>114-118</td>
<td>Violet</td>
</tr>
<tr>
<td>C</td>
<td>C_12H_10N_2O</td>
<td>Ethanol</td>
<td>72</td>
<td>155-161</td>
<td>Violet</td>
</tr>
<tr>
<td>A1</td>
<td>C_21H_18N_4OCl</td>
<td>Ethanol</td>
<td>63</td>
<td>Oil</td>
<td>Yellow</td>
</tr>
<tr>
<td>B1</td>
<td>C_14H_12N_3ClS</td>
<td>Ethanol</td>
<td>62</td>
<td>Oil</td>
<td>Nutty</td>
</tr>
<tr>
<td>C1</td>
<td>C_20H_16N_3ClO</td>
<td>Ethanol</td>
<td>64</td>
<td>Oil</td>
<td>Nutty</td>
</tr>
<tr>
<td>A2</td>
<td>C_21H_28N_4O</td>
<td>Ethanol</td>
<td>70</td>
<td>Oil</td>
<td>Yellow</td>
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<tr>
<td>B2</td>
<td>C_14H_17N_3S</td>
<td>Ethanol</td>
<td>73</td>
<td>Oil</td>
<td>Nutty</td>
</tr>
<tr>
<td>C2</td>
<td>C_20H_21N_3O</td>
<td>Ethanol</td>
<td>76</td>
<td>Oil</td>
<td>Nutty</td>
</tr>
</tbody>
</table>

General procedure for synthesis of compounds (A1) (B1) (C1)
A mixture of alcoholic solution with (A), with (B), with (C) (0.01 mol) and formaldehyde (15 ml, 40 %) was added slowly on alcoholic solution of (4-chloro-aniline ) (0.01 mol) the reaction mixture was stirred for three hours at room temperature and kept full night in the fridge. The solid obtained was filtered, washed with cold ethanol, dried and crystallized from aqueous ethanol to give compounds (A1), (B1), (C1).

General procedure for the synthesis of compounds (A2) (B2) (C2)
A mixture equimolar of (A), (B), (C) with Diallylamine in presence formaldehyde were carried out 0-5 °C by stirring with magnetic stirrer.

Scheme 1
RESULT AND DISCUSSION

The aim of the research is to synthesis manich bases from different Benzimidazole rings with primary and secondary amines by using formaldehyde as catalyst.

Infrared spectroscopy of this compound showed a broadband at 3348-3433 cm\(^{-1}\) refers to O-H group, as well as the emergence of weak peak at 1739 cm\(^{-1}\) indicate that O-H group turn to C=O.
group by resonance between O-H and N atom, the spectroscopy showed too other peaks at 3132-3178 cm⁻¹ refers to N-H group and at 3024 cm⁻¹ to C-H aromatic. Table (2) shows other peaks to this compound. ¹HNMR (400 MHz, DMSO) δ(ppm) Ar(6.97 Hz 1H), OH(5.45 Hz 1H), NH(5.45 Hz 1H)

1-[(4-chlorophenyl)amino][methyl]-1H-benzimidazol-2-ol (A1)

Infrared spectroscopy showed overlap of (O-H) peak with (N-H) peaks at 3261-3481 cm⁻¹ after substitution (H) atom by compound (4-chloro aniline), also emergence absorption peak at 2921-2979 cm⁻¹ refers to (C-H) aliphatic. Table (2) shows other peaks for this compound. ¹HNMR (400 MHz, DMSO) δ(ppm) Ar (7.09, 7.10 Hz and 7.25), OH(5.24 Hz), CH₂(5.77-5.81 Hz), NH(3.84-3.88 Hz).

1H-Benzimidazole-2-thiol (B)

Infrared spectrum for this compound showed appearance broadband at 3317-3417 cm⁻¹ indicate to (N-H) group, and appearance absorption peak at 3186 cm⁻¹ indicated to (C-H) aliphatic. Table (2) shows other absorption peaks for this compound. ¹HNMR (400 MHz, DMSO) δ(ppm) Ar(7.25-7.29 Hz and 7.32 Hz), OH(4.79 Hz), CH₂(4.68Hz), =CH(5.49-5.55 Hz), CH₂=CH(5.16-5.18 Hz).

1H-Benzimidazole-2-thiol (B1)

Infrared spectrum showed stay of absorption peaks of (N-H) group at 3224 cm⁻¹ after substitution of (H) atom by compound (4-chloroaniline) and emergence absorption peak at 2923 cm⁻¹ indicate to (C-H) aliphatic. Table (2) shows other absorption peaks for this compound. ¹HNMR (400 MHz, DMSO) δ(ppm) Ar(7.32, 7.44, 7.70, 7.79 Hz), OH(4.79 Hz), CH₂(4.68 Hz), CH₂=CH(5.16-5.18 Hz), =CH(5.49-5.55 Hz), CH₂=CH(3.67-369 Hz), =CH(5.49-5.55 Hz).
Fig. 1. F.T.I.R Spectroscopy of Compound (A)

Fig. 2. F.T.I.R Spectroscopy of Compound (A1)
Fig. 3. F.T.I.R Spectroscopy of compound (A1)

Fig. 4. F.T.I.R Spectroscopy of compound (B)
Fig. 5. F.T.I.R Spectroscopy of compound (B1)

Fig. 6. H-NMR Spectroscopy of compound (B2)
Fig. 7. H-NMR Spectroscopy of compound (C)

Fig. 8. H-NMR Spectroscopy of compound (C1)
CONCLUSION

In this study I am reported synthesis of many Benzimidazol rings from o-phenylenediamines as starting material with different compounds by using HCl as catalyst in all synthesis works and note the higher of percentage ratio for the results, then using Mannich reaction to prepared derivatives of the Benzimidazol rings were prepared. These derivatives confirmed from spectral data analysis; F.T.I.R and H-NMR.

ACKNOWLEDGEMENT

The author gratefully acknowledges Chemistry department, University of Al-Qadissiah, Iraq for providing lab facilities to carry out this work.

REFERENCE


Table. 2: Show F.T.I.R absorption packs of compounds

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<thead>
<tr>
<th>Compounds</th>
<th>C-H aryl</th>
<th>C=CC=N</th>
<th>C-N</th>
<th>C-O</th>
<th>C-S</th>
<th>C-Cl</th>
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<tbody>
<tr>
<td>A</td>
<td>3024</td>
<td>1670-1627</td>
<td>1361</td>
<td>1195</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>B</td>
<td>3093</td>
<td>1620-1496</td>
<td>1280</td>
<td>1195</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C</td>
<td>3055</td>
<td>1654-1612</td>
<td>1249</td>
<td>1157</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>A1</td>
<td>3066</td>
<td>1697-1683</td>
<td>1238</td>
<td>1093</td>
<td>---</td>
<td>632</td>
</tr>
<tr>
<td>B1</td>
<td>3039</td>
<td>1630-1596</td>
<td>1377</td>
<td>1190</td>
<td>605</td>
<td>825</td>
</tr>
<tr>
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<td>1616-1542</td>
<td>1272</td>
<td>1747</td>
<td>---</td>
<td>756</td>
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<tr>
<td>C2</td>
<td>3024</td>
<td>1662-1577</td>
<td>1218</td>
<td>1095</td>
<td>---</td>
<td>759</td>
</tr>
</tbody>
</table>

Fig. 9. F.T.I.R Spectroscopy of compound (C2)