Synthesis and Characterization of Some New Phenolic Schiff Bases Derivatives

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Abstract:
Starting from bis (4,4'-diamino phenoxy) ethan(1), a variety of phenolicschiff bases (methylolic, etheric, epoxy) derivatives have been synthesized. All proposed structure were supported by FTIR, $^{1}$H-NMR, $^{13}$C-NMR Elemental analysis, some derivatives evaluated by thermal analysis (TGA).

Keywords: phenoxy ethane, phenolic schiff bases.

Introduction:
The development of simple Synthetic routes to widely used organic compound using readily available reagents is one of the main objectives of organic Synthesis. The use of Schiff bases covered a wide area applications, in industry and biological field[1]. In industry (phenolic, methylolic, epoxy) Schiff bases were used as a rubber accelerators[2], antioxidants[3] and corrosion inhibitors[2]. They have wide industrial applications as photostabilizers for polyethylene. In analytical chemistry Schiff bases were used for uptake of metal ions[4], and the methylolic resins of some phenolic Schiff bases are used in the accurate determination of trace elements in dilute solution, which is often hindered due to the sensitivity limits of the equipment used for the purpose[5], in this study number of methylolic, etheric and epoxy Schiff bases[6] were prepared from condensation reaction of aromatic aldehyde with [bis(4,4- dianminophenoxy) ethane], the methylolic, etheric and epoxy resins were prepared through condensation with formaldehyde, alcohol, eipychlorohydrine and piperdine, respectively.

Materiala and Methods:
General
Melting points were determined on Gallen kamp, melting point apparatus and were uncorrected. FTIR spectra of the compounds were recorded on a (SHIMADZU) FTIR, 8300 Spectrometer as KBR-disc, $^{1}H - NMR$, $^{13}$C-NMR spectra were recorded at 200.13-50.32 $^{MH_{4}}$, respectively using tetra methyl Silane (TMS) as an internal standard, (DMSO as a solvent. Elemental analysis were run using a perkin-Elmer RE 2400 (C.H.N) analyzer, thermal stability TGA. All analysis were performed in center of consultation/ University of Jordan.

Materials
All the chemical used were supplied by (Merk, Fluka and BDH) chemicals, the solvents purified by distillation and dried with calcium chloride.

Measurement and Techniques
The purity of products were investigated by (T.L.C) technique by using a mixture of benzene – ethanol (5:5 v/v) as elute and iodine chamber for spot location.

Thermal graviemetric Analysis (TGA)
Curing of the prepared Schiff bases resins were evaluated by using (thermogravimetric analysis TGA using (NETZSCHESTA/409-PG/PC. Mode/ Type of Meas (DTA-TG). The programmed heating rate of 20oC/ min from (25-1000) oC under inter atmosphere (N2 gas). So that heat lost or absorbed were recorded fig (15-18) and analyzed table (4).

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Synthesis Bis (4,4'- diamino phenoxy) ethane (1) [7]:
Alcoholic sodium hydroxide (0.2mol, 8gm) in 20m/abs. ethanol with (0.02mol, 2.91gm) (p-hydroxy aniline).
To mix admixture until all the solid dissolved, then solve with (0.01mol, 0.64ml) (dibromo ethane). Refluxing 3h, the solute to a pour for groats ice, the solute to come into Being, filtered and recrystallized in ethanol (m.p 238 – 240 °C) solid, violet.

Synthesis of phenolic Schiff base (2) [6]:
Phenolic Schiff base [2] were prepared by well established procedure in the literature[8], condensing (0.02mol, 4.9gm) compound (1) with (0.04mol, 4.9gm) p-hydroxy benzaldehyde, the purity of the products were investigated by T.L.C (m.p 212 – 214 °C) solid, red..

Synthesis of methylolic phenolic Schiff base resin (3) [8]:
A250ml necks round bottomed flask equipped with mechanical stirrer, condenser and thermometer, the flask was immersed in water bath, then charged with (0.05mol) of phenolic schiff base [2] and (0.05mol, 1.5ml) formaldehyde solution (41-37)% in 50ml (THF) tetrhydrofuran, the reactants were then mixed gently with ethanolic sodium hydroxide solution (10%) was added portion wise to kept the PH of the reaction mixture (9-10), then gently added (0.14mol) alcoholic sodium hydroxide in two portions with kept the temperature below (60-65) °C. The stirring continued for 2h, after first addition the aqueous layer was separated from the organic layer, the second portion of NaOH solution and stirred further for 1h, then left the mixture at the same temperature for (50min), and also the aqueous was separated. The organic layer was dried and excess of (eipychlorohydride) and solvent distilled off under reduced pressure. The formed resins were purification by T.L.C.

Synthesis of etheric methylolic Schiff base (4-6) [9]:
To mix an appropriate alcohol (CH$_3$OH, C$_3$H$_7$OH, C$_4$H$_9$OH) respectively (0.08mol) with (1ml) concentration (H$_2$SO$_4$) at groats ice (0-2) °C, an appropriate methylolich Schiff base [3] (0.4mol) which added gently to the mixture about 1h, Refluxing and increased the temperature gradually to the boiling point of alcohol used, the mixture were kept at boiling alcohol for 24h, then neutralized the cooled mixture by using Sodium hydroxide. The resins formed was extracted using chloroform (CHCl$_3$), dried and evaporated under vacuum, purity by T.L.C.

Synthesis of epoxy phenolic Schiff base (7-10) [10,11] :
To a mixture of an appropriate (0.01mol) phenolic Schiff bases [4-6] with (0.12mol) (eipychlorohydrine ) at ice water (0-5) °C for (15min), then gently added (0.14mol) alcoholic sodium hydroxide in two portions with kept the temperature below (60-65) °C. The stirring continued for 2h, after first addition the aqueous layer was separated from the organic layer, the second portion of NaOH solution and stirred further for 1h, then left the mixture at the same temperature for (50min), and also the aqueous was separated. The organic layer was dried and excess of (eipychlorohydride) and solvent distilled off under reduced pressure. The formed resins were purification by T.L.C.

Synthesse schiff bases resins with unstitched ring (11-14) [11]:
A mixture of (0.01mol) epoxy [7-10] in (30ml) (1-2) °C Cold methanol with (0.015mol) piperidine. Refluxing in oil bath (80-100) °C for (72h), after cooling the solvent evapourated and purification by T.L.C.
All these synthesis steps were summarized in schemes (1-6), physical properties, FTIR, ($^1$H, $^{13}$C – NMR ), elemental analysis, thermal stability (TGA) are listed in tables (1-5), respectively, some compounds evaluated clearly show the temperature rate belong different type dissociation were recorded fig (1-4).

Results and Discussion:
Considerable interests have been expressed in synthesis of schiff bases in recent year due
to their industrial and biological importance, starting from [bis (4,4'-diaminophenoxy)ethane](1)

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{OH} + \text{Br(C}_2\text{H}_4\text{)Br} \\
\text{NaOH} \rightarrow \text{EtOH}
\end{array}
\]

\[\text{(1)}\]

Scheme -1-

The FTIR spectrum [13,14] showed the strong stretching vibration (3420-3375) cm\(^{-1}\) due to \((NH_2)\) groups, (2930-2860) cm\(^{-1}\) for \((CH_2)\), (1260-1045) cm\(^{-1}\) for (c-o-c), (830) cm\(^{-1}\) for (1,4-disubst), (3080) cm\(^{-1}\) for (Ar-H), (1420) cm\(^{-1}\); for (C-N); 1H-NMR (DMSO-d6) \(\delta: (7.4-7.6)\) ppm due to (Ar-H), (8.5-6.2) ppm due to (2H,NH2), (1.42-2.81) ppm for (2H,CH2); 13C-NMR (DMSO-d6) \(\delta: (72.4-72.8)\) ppm for (C-O-C), (128.2-129.3) ppm due to (aromatic carbons), (143.1-144.6) ppm for (Ar-NH2). Elemental analysis (C,H,N) for compound (1) were fitted according to the (table 3).

Therefore schiff base (2) prepared by the condensation of the corresponding compound (1) with (p-hydroxybenzaldehyde in refluxing ethanol.

\[
\begin{array}{c}
\text{H}_2\text{N} \quad \text{OC}_2\text{H}_4\text{O} \quad \text{NH}_2
\end{array}
\]

\[\text{(2)}\]

Scheme -2-

The reaction proceeds by the nucleophilic attachment of the nucleophilic nitrogen atom of the amine on the carbonyl group of aldehyde with the loss of water molecular to give a stable compound in good yield, the FTIR spectrum showed the strong bands (1602) cm\(^{-1}\) for (C=N) combined with disappearance of stretching bands (3420-3325) cm\(^{-1}\) of (NH2), strong bands (3400-3240) cm\(^{-1}\) for (OH) and (1150-1160) cm\(^{-1}\) absorption bands for phenolic group (C-O); 1H-NMR (DMSO-d6) \(\delta: (7.73-7.85)\) ppm for (Ar-H), (10.12-10.16) ppm (H,OH); 13C-NMR (DMSO-d6) \(\delta: (128.2-128.9)\) ppm (aromatic carbons), (115.2-117.2) ppm for (C,=CH), (148.5-152.6) ppm for (C=N), (155.1-156.0) ppm for (Ar-OH). Elemental analysis for compound (2) were fitted according to the (table 3). Refluxing compound (2) with formaldehyde afforded methylolic resins (3) which consisting of hydroxyl methylene group (-CH2OH) known as a methylol groups which are chemically very reactive functional groups:
Compound (3) indicated by (FTIR) spectrum of abroad stretching bands at (3417-3265) cm\(^{-1}\) for methyolic groups combined with strong stretching bands at (2954-2896) cm\(^{-1}\) for aliphatic (CH\(_2\)) ; 1H-NMR(DMSO-d6) \(\delta\): (7.20-8.10) ppm due to (Ar-H), (10.62-10.89) ppm for (H,OH), (1.06-2.90) ppm for (t,2H,CH\(_2\)) ; 13C-NMR(DMSO) \(\delta\): (126.5-126.8) ppm (aromatic carbons), (120-124) ppm for (C=CH), (154.8-154.9) ppm for (Ar-OH). Emental analysis for compound (3) were fitted according to the (table 3).

Compound (3) similarly reacts with (methanol propanol, Butanol) afforded etheric resins (4-6):

\[
\text{R} = -\text{CH}_3, -\text{C}_3\text{H}_7, -\text{C}_4\text{H}_9
\]

Compound [4] indicated in FTIR spectrum of stretching vibration is more sharp bands at (2980-2975) cm\(^{-1}\) for (CH\(_2\)) and strong vibration at (1226-1168) cm\(^{-1}\) for (C-O-C); 1H-NMR(DMSO-d6) \(\delta\): (7.3-7.6) ppm due to (Ar-H), (2-2.2) ppm for (3H, CH\(_3\)), (10.01-10.21) ppm for (H,OH); 13C-NMR(DMSO-d6) \(\delta\): ((11.5-116.4) ppm due to (aromatic carbons), (149-151) ppm due to (C=\(\text{N}\)), (154.2-154.9) ppm due to (Ar-OH), 972.1-72.6 ppm for (C-O-C). Emetal analysis for compound [4] were fitted according to the (table 3). Similarly react compounds (4-6) with eipychlorohydrine afforded (7-9) derivatives respectively.

\[
\text{R} = -\text{CH}_3, -\text{C}_3\text{H}_7, -\text{C}_4\text{H}_9
\]
Compound (7) obtained FTIR spectrum for sharp bands for oxarine absorption at (948-995) cm\(^{-1}\) and strong bands (2931-2873) cm\(^{-1}\) for (CH\(_2\)), (1130-1090) cm\(^{-1}\) for (C-O-C); 1H-NMR(DMSO-d6) \(\delta\): (7.2-7.5)ppm for (Ar-H), (1.9-2.1)ppm due to (3H, CH\(_3\)); 13C-NMR (DMSO-d6) \(\delta\): (129.3-130.1)ppm due to (aromatic carbons), (2.1-2.3)ppm for (CH\(_2\), oxarine), (72.6-72.9)ppm due to (C-O-C).

Elemental analysis for compounds (7) were fitted according to the (table 3). Finally (7-9) compounds react with piperdine a corresponding (10-12) respectively.

(R = -CH\(_3\), -C\(_3\)H\(_7\), -C\(_4\)H\(_9\))

![Scheme 6](image)

The FTIR spectrum of compound (10) obtained increasing in stretching vibration of (OH) at (3479-3437) cm\(^{-1}\) and (1220-1225) cm\(^{-1}\) for (C-O), (1268-1238) cm\(^{-1}\) due to (C-O-C); 1H-NMR(DMSO-d6) \(\delta\): (7.8-7.9)ppm due to (Ar-H), (9.7-9.8) due to (H,OH), (1.39-1.41)ppm for (2H,CH\(_2\)); 13C-NMR(DMSO-d6) \(\delta\): (72.8-72.9)ppm due to (C-O-C), (129.3-130.1)ppm for (aromatic carbons).

Elemental analysis for compounds [10] were fitted according to the (table 3). All these steps were summarized in schemes (1-6) physical properties of all mentioned and other details [FTIR, Elemental analysis, TGA, analysis, 1H-NMR, 13C-NMR,] , data are listed in tables (1-5) respectively, curing thermal stability of some compounds were evaluated by using (TGA) table (4) is clearly show the temperature rate belong to different type dissociated for derivatives, fig(15-18).
Table (1) Dapcited physical properties for (1-12) compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecular formula</th>
<th>M.P</th>
<th>Colour</th>
<th>Yield %</th>
<th>Purification solvent</th>
<th>Comp No.</th>
<th>Molecular formula</th>
<th>M.P</th>
<th>Colour</th>
<th>Yield %</th>
<th>Purification solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C14H16N2O2</td>
<td>238-240</td>
<td>Pale violet</td>
<td>90</td>
<td>Ethanol</td>
<td>7</td>
<td>C42H42N2O1</td>
<td>0</td>
<td>Oily</td>
<td>60</td>
<td>THF</td>
</tr>
<tr>
<td>2</td>
<td>C28H24N2O4</td>
<td>212-214</td>
<td>Deep Red</td>
<td>87</td>
<td>Ethanol</td>
<td>8</td>
<td>C42H45N2O1</td>
<td>0</td>
<td>Oily</td>
<td>65</td>
<td>THF</td>
</tr>
<tr>
<td>3</td>
<td>C32H32N2O8</td>
<td>Oily</td>
<td>Brown</td>
<td>80</td>
<td>THF</td>
<td>9</td>
<td>C54H42N2O1</td>
<td>0</td>
<td>Oily</td>
<td>60</td>
<td>THF</td>
</tr>
<tr>
<td>4</td>
<td>C36H40N2O8</td>
<td>Oily</td>
<td>Brown</td>
<td>75</td>
<td>THF</td>
<td>10</td>
<td>C52H66N4O1</td>
<td>0</td>
<td>Oily</td>
<td>70</td>
<td>Methanol</td>
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<tr>
<td>5</td>
<td>C44H54N2O2</td>
<td>Oily</td>
<td>Brown</td>
<td>75</td>
<td>THF</td>
<td>11</td>
<td>C60H66N2O1</td>
<td>0</td>
<td>Oily</td>
<td>72</td>
<td>Methanol</td>
</tr>
<tr>
<td>6</td>
<td>C48H64N2O2</td>
<td>Oily</td>
<td>Brown</td>
<td>65</td>
<td>THF</td>
<td>12</td>
<td>C64H94N2O1</td>
<td>0</td>
<td>Oily</td>
<td>65</td>
<td>Methanol</td>
</tr>
</tbody>
</table>

Table (2) FTIR spectral data of (1-12)

<table>
<thead>
<tr>
<th>No.</th>
<th>VOH</th>
<th>VCH2</th>
<th>VC-O- C</th>
<th>VC-O</th>
<th>Others</th>
<th>No.</th>
<th>VOH</th>
<th>VCH2</th>
<th>VC-O- C</th>
<th>VC-O</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>2930</td>
<td>2910</td>
<td>1260</td>
<td>-</td>
<td>7</td>
<td>3257</td>
<td>3225</td>
<td>2931</td>
<td>2873</td>
<td>1201</td>
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<tr>
<td>2</td>
<td>3400</td>
<td>2860</td>
<td>1200</td>
<td>1212</td>
<td>1228</td>
<td>8</td>
<td>3290</td>
<td>3155</td>
<td>2910</td>
<td>2875</td>
<td>1202</td>
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<tr>
<td>3</td>
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<td>1235</td>
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<tr>
<td>4</td>
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<td>2980</td>
<td>1260</td>
<td>1168</td>
<td>1197</td>
<td>10</td>
<td>3479</td>
<td>3437</td>
<td>2900</td>
<td>2865</td>
<td>1268</td>
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<tr>
<td>5</td>
<td>3285</td>
<td>2985</td>
<td>1218</td>
<td>1210</td>
<td>1100</td>
<td>11</td>
<td>3310</td>
<td>3260</td>
<td>2910</td>
<td>2845</td>
<td>1250</td>
</tr>
<tr>
<td>6</td>
<td>3290</td>
<td>2968</td>
<td>1220</td>
<td>1214</td>
<td>1113</td>
<td>12</td>
<td>3316</td>
<td>3280</td>
<td>2900</td>
<td>2886</td>
<td>1260</td>
</tr>
</tbody>
</table>

Table (3) Depacited Elemental analysis (C.H.N) for some compounds.

<table>
<thead>
<tr>
<th>No.</th>
<th>(C.H.N) analysis calculated (found)</th>
<th>Comp No.</th>
<th>(C.H.N) analysis calculated (found)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>68.89 (69.20) 6.56 (7.53) 11.48 (12.68)</td>
<td>4</td>
<td>72.48 (73.39) 6.71 (7.90) 4.70 (5.69)</td>
</tr>
<tr>
<td>2</td>
<td>74.34 (75.41) 5.31 (6.30) 6.20 (6.98)</td>
<td>7</td>
<td>68.67 (69.93) 5.72 (6.91) 3.82 (4.91)</td>
</tr>
<tr>
<td>3</td>
<td>67.13 (68.20) 5.59 (6.60) 4.90 (5.95)</td>
<td>10</td>
<td>68.87 (69.86) 7.29 (8.28) 6.18 (7.18)</td>
</tr>
</tbody>
</table>

Table (4) Show the Curing temperature of some Compounds

<table>
<thead>
<tr>
<th>Comp No.</th>
<th>Primary dissociated</th>
<th>Finally dissociated</th>
<th>50% dissociated</th>
<th>Maximum dissociated</th>
<th>Average dissociated</th>
<th>% Char content</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>220</td>
<td>380</td>
<td>350</td>
<td>310</td>
<td>0.25</td>
<td>93.77</td>
</tr>
<tr>
<td>4</td>
<td>225</td>
<td>400</td>
<td>300</td>
<td>280</td>
<td>0.12</td>
<td>92.73</td>
</tr>
<tr>
<td>7</td>
<td>180</td>
<td>750</td>
<td>612</td>
<td>325</td>
<td>0.06</td>
<td>61.63</td>
</tr>
<tr>
<td>10</td>
<td>165</td>
<td>260</td>
<td>700</td>
<td>660</td>
<td>0.053</td>
<td>58.70</td>
</tr>
</tbody>
</table>
Table (5) 1H-NMR and 13C-NMR spectral data for some compounds.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound Structure</th>
<th>1H-NMR/ data</th>
<th>13C-NMR/ data</th>
<th>No</th>
<th>Compound Structure</th>
<th>1H-NMR/ data</th>
<th>13C-NMR/ data</th>
</tr>
</thead>
</table>
| 1  | ![Structure 1](image1) | δ: 7.4-7.6 (Ar-H)  
δ: 8.5-6.2 (2H, NH2)  
δ: 1.42-2.81 (2H, CH2) | δ: 72.4-72.8 (C-O-C)  
δ: 128.2-129.3 (aromatic carbons)  
δ: 143.1-144.6 (Ar-NH2) | 4 | ![Structure 4](image4) | δ: 7.3-7.6 (Ar-H)  
δ: 2-2.1 (3H, CH3)  
δ: 10.01-10.21 (H, OH) | δ: 115.2-116.2 (aromatic carbons)  
δ: 149-151 (C=N)  
δ: 154.2-154.9 (Ar-OH)  
δ: 72.1-72.6 (C-O-C) |
| 2  | ![Structure 2](image2) | δ: 7.73-7.85 (Ar-H)  
δ: 10.12-10.16 (H, OH) | δ: 128.2-128.9 (aromatic carbons)  
δ: 115.2-117.2 (C=CH)  
δ: 148.5-152.6 (C=N)  
δ: 155.1-156 (Ar-OH) | 7 | ![Structure 7](image7) | δ: 7.2-7.5 (Ar-H)  
δ: 1.9-2.1 (3H, CH3) | δ: 129.3-130.1 (aromatic carbons)  
δ: 2.1-2.3 (CH2, oxarine)  
δ: 72.6-72.9 (C-O-C) |
| 3  | ![Structure 3](image3) | δ: 7.20-8.10 (Ar-H)  
δ: 10.62-10.89 (H, OH)  
δ: 1.06-2.90 (2H, CH2) | δ: 126.5-126.3 (aromatic carbons)  
δ: 120-124 (C=CH)  
δ: 154.8-154.9 (Ar-OH) | 10 | ![Structure 10](image10) | δ: 7.8-7.9 (Ar-H)  
δ: 9.7-9.8 (H, OH)  
δ: 1.39-1.41 (2H, CH2) | δ: 72.8-72.9 (C-O-C)  
δ: 129.3-130.1 (aromatic carbons) |
Fig. (1) FT-IR for compound (1)

Fig. (2) FT-IR for compound (2)

Fig. (3) FT-IR for compound (3)

Fig. (4) FT-IR for compound (4)

Fig. (5) FT-IR for compound (7)

Fig. (6) FT-IR for compound (10)
Fig. (7) HNMR Spectrum of Compound (1)

Fig. (8) HNMR Spectrum of Compound (4)

Fig. (9) HNMR Spectrum of Compound (7)

Fig. (10) HNMR Spectrum of Compound (10)
Fig. (11) $^{13}$CNMR Spectrum of Compound (1)

Fig. (12) $^{13}$CNMR Spectrum of Compound (4)

Fig. (13) $^{13}$CNMR Spectrum of Compound (7)

Fig. (14) $^{13}$CNMR Spectrum of Compound (10)
تحضير وتشخيص بعض مشتقات قواعد شيف الفينولية

إيمن مهدي محمد حسن
سناء هاشم صالح

كلية العلوم للبنات / جامعة بغداد / قسم الكيمياء

*الخلاصة:

ابتداءً من المركب (4 و/4ثنائي أمين فينوكسي) ابتทาน(1) ، حضرت عدد من مشتقات قواعد شيف الفينولية

(الميثيلولية، الأثيرية، الإيبوكسية) ..............

لقد تم تشخيص المركبات الجديدة بمطيافية الأشعة تحت الحمراء وطيف الرنين المغناطيسي -1H,13C-

والتحليل الكمي الدقيق للعناصر (C,H,N) مع قياس آلية الثبات الحراري باستعمال تقنية التحليل NMR و

الحراري الوزني TGA.

References: