KNOEVENAGEL CONDENSATION OF 5-SUBSTITUTED FURAN-2-CARBOXALDEHYDE WITH INDAN-1,3-DIONE

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Abstract
A series of new heterocyclic compounds of 2-(5-substituted -Furfurylidene)-Indane-1,3-dione, were prepared and identified by their melting points, Infrared, Ultraviolet, and Nuclear magnetic resonance spectrums.

Key words: Knoevenagel condensation, Furfurylidene, Indan-1,3-dione

Introduction:
One of the most important objects of knovenagel condensation from a synthetic perspective is that they offer a route to the formation of C=C bond, by which the arylidene compounds are obtained from carbonyl compounds and active methylene compounds[1-3], in the presence of basic catalyst or lewis acid catalyst, such as piperidine, diethylamine, or corresponding ammonium salt.[4-8]. In recent years there has been an growing interest in knovenagel condensation products because many of them have significant biological activity[9-13]. This reaction has been widely used in organic synthesis to prepare cumarins and its derivatives, which are important intermediates in the preparation of cosmetics, perfumes, and pharmaceuticals [14,15]. Furfural and its 5-substituted derivatives were chosen as being synthetically versatile molecules with a reactive carbonyl group, they have considerable significance for their biological activities[16-19] and for their reactivity toward Nucleophiles which allows the synthesis of a wide variety of heterocyclic such as nifuroxazide(NF) (condensation of 5-nitro furfural with p-hydroxybenzhydrazide)[20]. This is used for the treatment of acute bacterial diarrhea[21]. In addition to that, β-dicarbonyl compounds have been studied intensively owing to their synthetic and biological significance and as well known indan-1,3-dione derivatives are important as anticoagulant drugs or rodenticides inhepete.[22] In addition to anticoagulant effect and rodenticidal activity. These compounds have shown parasiticidal effects.[23] Analgesic, herbicidal[24]. This work involve preparation and identification of some new substituted
Furfurylidine indan-1,3-dione a heterocyclic derivatives of Furfural.

**Experimental**

Prepared compounds were characterized by UV,$^1$H-NMR and IR spectra Table (1-3). The melting points were determined on a Kofler Block apparatus and are uncorrected. Infrared spectra were recorded in 400 - 4000 cm$^{-1}$ region by a Specord FT-IR Jusco 300 spectrometer using KBr disk. $^1$H-NMR Spectra were measured on ambient Broker DT-400 MHz spectrometer in deuterated CDCl$_3$, and UV-visible were determined with Shimadzu 190 A spectrometer(College of Science - Damascus University). All fine chemicals and reagents were purchased from Aldrich chemical Co. U.S.A. Furfural were pre-distilled and dried appropriately prior to use.

### Synthesis of 3a-3d

A mixture of 5-substituted-furfural 1a-1d (5 mmol), Indan-1,3-dione (2) (5 mmol) in ethanol (10 cm$^3$) and (10 cm$^3$), was stirred with simple heating until the solid was dissolved then stirred at room temperature for the time given in Table (1). The solid precipitate was filtered. The products were recrystallized from ethanol or acetic acid.

### Results and Discussion

A four-(5-substituted furfurylidene) Indane-1,3-diones(3a-3d) were obtained by condensations of some 5-substituted Furfural (1a-1d) with Indane-1,3-diones (2) in ethanol, at room temp. The yield of prepared compounds were ranged between (46-72%). Table (1) show some properties of these compounds.

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Where R=a: H , b: C2H5 , c: I , d :NO2
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$^1$H-NMR spectra of these compounds [Figs 1-4], indicate a disappearance proton signals at δ(4.10 ppm for the (methylene and aldehyde groups) of compounds(1 and 2) and appearance of a proton signal of olifene α-proton ( $H_α$) [structure 4] at (7.7-7.8) ppm for all prepared compounds. Also $^1$H-NMR spectral analysis shows proton signals of aromatic and furan rings at δ (6.4-8.6) ppm as in (Table 2). All condensation products are stable solid compounds, rather insoluble in common solvents, with high melting points. The resonance signals and their multiplicity confirmed the proposed structures. The infrared spectra of the prepared compounds (3a-3d) showed strong absorption bands of the C=C and C=O stretching vibrations in two very well distinguished regions (1610 - 1680) cm$^{-1}$ and (1690-1758) cm$^{-1}$ (Table 3). The absorption bands in the lower region of the spectra(1400-1600) cm$^{-1}$ belong to the $\nu$(C=C) of the furan and aromatic-rings. The compound 3d showed the v(C=C) band at a lower frequency (1627)cm$^{-1}$, due to the presence of withdrawing nitro group and its conjugation effect with furan ring [25]. (Table 1). UV spectra showed red-shift phenomena for all prepared compounds attributed to the conjugated of furan ring with C=C bond formed, table (1). Where $\lambda_{max}$ for furfural is(329nm) while $\lambda_{max}$ for indan is (358nm).
Table 1: Characterization of the prepared compounds

<table>
<thead>
<tr>
<th>Comp.</th>
<th>R</th>
<th>NO.of gm. used</th>
<th>Formula</th>
<th>M.wt</th>
<th>m.p. °C</th>
<th>Colore</th>
<th>Yield %</th>
<th>Tr(Stirr.) (hr)</th>
<th>( \lambda_{\text{max}}, \text{nm} ) Fu.r,indan</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>H</td>
<td>0.48</td>
<td>C_{14}H_{8}O_{3}</td>
<td>224.21</td>
<td>203-205</td>
<td>yellow</td>
<td>50</td>
<td>2.5</td>
<td>366,390</td>
</tr>
<tr>
<td>3b</td>
<td>C_{2}H_{5}</td>
<td>0.62</td>
<td>C_{14}H_{10}O_{3}</td>
<td>252.26</td>
<td>105-107</td>
<td>yellow</td>
<td>46</td>
<td>5</td>
<td>395,398</td>
</tr>
<tr>
<td>3c</td>
<td>I</td>
<td>0.89</td>
<td>C_{14}H_{10}O_{3}</td>
<td>350.11</td>
<td>195-197</td>
<td>Dark yellow</td>
<td>68</td>
<td>3</td>
<td>396,405</td>
</tr>
<tr>
<td>3d</td>
<td>NO_{2}</td>
<td>0.7</td>
<td>C_{14}H_{8}NO_{5}</td>
<td>269.21</td>
<td>189-191</td>
<td>Pale orange</td>
<td>72</td>
<td>0.75</td>
<td>372,385</td>
</tr>
</tbody>
</table>

Table 2: \(^1\)H NMR spectral data of prepared compounds in CDCl\(_3\)

<table>
<thead>
<tr>
<th>COMP.</th>
<th>(^1)H NMR spectrum ppm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>( \delta:7.78 ) (s,1H,Ha); 7.78,7.79-7.82,8.61 (7H,4H-ArH,3H-furan ring).</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>( \delta:1.35 ) (t, 3H-C_{2}H_{5}); 2.83 (q, 2H, -C_{2}H_{5}); 7.73 (s, 1H, Ha); 6.43,7.77-7.78,7.97-7.98,8.6 (6H,4H-arom.and 2H-furanes) 8.59</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>( \delta:7.72(s,1H,Ha);6.92,7.79-7.82,7.97-8.00,8.46(6H,4H-arom.and 2H furanes).</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>( \delta:7.72(s,1H,c=cHo);7.50,7.88-7.91,8.05-8.08,8.62(6H,4H-arom.and 2H-furanes).</td>
<td></td>
</tr>
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</table>

Table 3: IR spectral data of synthesized compounds 3a-3d.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>( \nu\text{C}=\text{O} )</th>
<th>( \nu\text{C} = \text{C furan,Ar} )</th>
<th>( \nu\text{C} = \text{C} )</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>1745,1695</td>
<td>1412,1570</td>
<td>1680</td>
<td></td>
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<tr>
<td>3b</td>
<td>1758,1700</td>
<td>1413-1562,1590</td>
<td>1653</td>
<td>CH aliphatic, 2932</td>
</tr>
<tr>
<td>3c</td>
<td>1720,1690</td>
<td>1425,1540,1580</td>
<td>1610</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>1730,1690</td>
<td>1400,1470,1590</td>
<td>1627</td>
<td>NO_{2};1348,1517,[26].</td>
</tr>
</tbody>
</table>
Figure 3: $^1$H NMR spectrum of comp.3c

Figure 4: $^1$H NMR spectrum of comp.3d5654er
References


Figure 5: IR spectrum of comp.3a

Figure 6: IR spectrum of comp.3d


