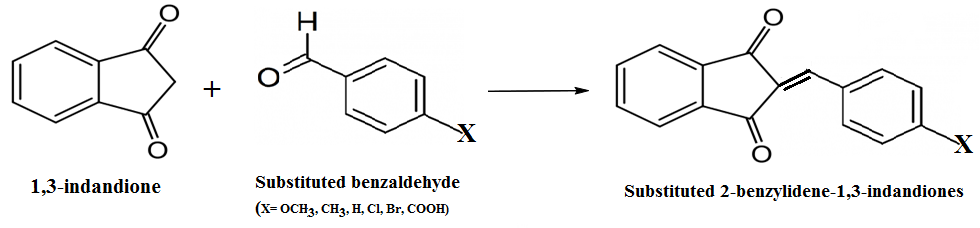
Chapter 2. Experimental section

**2. Experimental section**

The details of the preparation and characterization of *p*-substituted 2-benzylidene-3-indandiones, *p*-substituted 5-benzylidenebarbituric acids and *p*-substituted (E)-1-(furan-2-yl)-3-phenylprop-2-ene-1-ones and the details of the measurements of the UV, IR and electrochemical data are described in this chapter.

**2.1 Preparation of *p*-substituted 2-benzylidene-3-indandiones.**

2-benzylidene-3-indandione and its substituted compounds were prepared by the reported procedure69sk. To the calculated amount of the appropriate benzaldehyde (12.5 mM) and 1,3-indandione (12.5 mM) in warm ethyl alcohol was added a 10% solution of sodium hydroxide (catalytic amount) and the reaction mixture stirred for 2 h to 3 h and left overnight (Scheme 2.1). The solvent was removed under vacuum. The resulting crude product was purified by column chromatography.

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Scheme 2.1

**2.2 Characterization**

All chemicals used were purchased from Sigma Aldrich. The purity of the compounds was checked by TLC on silica gel G plates. All the compounds were characterized as 2-benzylidene-3-indandione and its derivatives (Fig.2.1) by UV-Visible, FT-IR and NMR spectral techniques. UV-Visible spectra were recorded on a CARY VARION (V 550), CHCl3 was used as a solvent. Infrared spectra were obtained on a PARAGON 500 spectrometer on KBr pellets. 1H and 13C spectra were obtained on a BRUKER AMX 400 MHz spectrometer. The chemical shift of 1H was measured with the peak of CDCl3 at δ 7.29 as the internal reference, while those of 13C were recorded with the central peak of CDCl3 at δ 77.03 as the internal reference.



Fig. (2.1)

Where X is the substituents viz. OMe, Me, H, Cl, Br, and COOH

**2.2.1 UV-visible spectral characterization**

UV-Visible absorption spectra were recorded for all the compounds and CHCl3 was used as a solvent. UV-Visible absorption spectra of the substituted 2-benzylidene 1,3 indandiones are given in Figs. (2.2 – 2.7). λmax values for various *p*-substituted 2-benzylidene-3-indandiones are given in Table (2.1).

Table (2.1): λmax values for various *p*-substituted 2-benzylidene-3-indandiones in CHCl3.

|  |  |  |
| --- | --- | --- |
| S.No. | Substituent X | Observed λCHCl3  nm |
|  |  |  |
| 1. | *p*-OCH3 | 525,386 |
| 2. | *p*-CH3 | 264,357 |
| 3. | H | 264,345 |
| 4. | *p*-Cl | 265,351 |
| 5. | *p*-Br | 265,353 |
| 6. | p-COOH | 263,340 |
|  |  |  |

**2.2.2. FT-IR Spectra Characterization**

FT-IR spectra of *p*-substituted 2-benzylidene-3-indandiones are shown in figures

(2.8 - 2.13). FT-IR (KBr pellets) data for the above compounds are given below.

1. **2-(4’-methoxybenzylidene)-1,3-indandione:** 3439.07, 2839.62,1581.14, 1555.70, 1505.89, 1266.32, 1174.91, 1022.34, 839.46, 731.99, 526.21.
2. **2-(4’-methylbenzylidene)-1,3-indandione:** 3489.89, 1725.29,1683.93, 1588.08, 1373.46, 1351.89,1332.42, 1189.24,1080.52, 989.52,818.12,739.74.
3. **2-benzylidene-1,3-indandione:** 3783.09,3063.50,2364.96,1724.93,1683.75,1586.17,

1376.53,1345.96,1244.02,1198.94,981.07,732.69,682.38,568.09.

4. **2-(4’-chlorobenzylidene)-1,3-indandione:** 3696**.**20,3092.11,2363.08, 1726.37,

1689.99, 1609.80, 1582.35, 1486.02, 1411.93, 1203.63, 1092.42,1074.32, 830.56.

5. **2-(4’-bromobenzylidene)-1,3-indandione:** 3086.69, 1726.98, 1689.61, 1612.90,

1577.50, 1408.55, 1485.35, 1248.20,1202.37,1162.92,1072.53,828.32,736.35.

6. **2-(4’-carboxybenzylidene)-1,3-indandione:** 2825.28,2549.02, 1731.80, 1687.05,

1618.67,1592.13, 1428.79, 1293.26, 1248.65, 1202.53, 1156.73, 988.89, 734.01.

**2.2.3. Assignment of 1H NMR Chemical shifts**

In 1H NMR spectra of 2-benzylidene1,3-indandione whose signals assignment were quite complicated, but the ethylene proton is well separated from the signals of the aromatic protons because of the β-proton nearest to the aromatic ring will experience a magnetic field from the induced circulation of π-electrons in the aromatic ring, which will augment the applied field and hence will lead to downfield shift.

All the aromatic protons are deshielded because of ring current effect. Assignment of the signals was based on splitting pattern and peak integration ratio. 1H NMR spectra of substituted 2-benzylidene 1,3-indandiones are given in Figs. (2.14 – 2.19). 1H NMR chemical shift data for

2-benzylidene 1,3-indandiones are given below.

1. **2-(4’-methoxybenzylidene)-1,3-indandione: δ** 3.917(s,3H), 6.998-7.027(m,2H), 7.766-7.842(m,2H), 7.842(s,1H),7.958-8.000(m,2H), 8.529-8.558(m,2H).
2. **2-(4’-methyibenzylidene)-1,3-indandione: δ** 2.343(s,3H),7.178(d,2H),

7.689-.710(m,2H), 7.766(s,1H), 7.899(dd,1H), 8.287(d,1H).

3. **2-benzylidene-1,3-indandione: δ** 7.519-7.580(m,4H), 7.824-7.846(m,2H), 7.9249(s,1H),

8.020-8.047(m,2H), 8.465-8.4869(dd,2H).

4. **2-(4’-chlorobenzylidene)-1,3-indandione: δ** 7.474-7.495(m,2H), 7.834-7.848(m,2H),

7.827(s,1H), 7.997-8.018(m,2H), 8.417-8.438(m,2H).

5. **2-(4’-bromobenzylidene)-1,3-indandione: δ** 7.640-7.662(dd,2H), 8.322-8.353(dd,2H),

7.811(s,1H), 8.011-8.035(m,2H), 7.829-7.851(m,2H).

6. **2-(4’-carboxybenzylidene)-1,3-indandione: δ** 7.851(s,1H), 7.902-7.923(m,2H), 7.955-

7.992(m,2H), 8.039(d,2H), 8.465(d,2H).



**Fig. 2.14. 1H NMR spectrum of** **2-(4’-methtoxybenzylidene)-1,3-indandione**



**Fig.2.15**. **1H NMR spectrum of** **2-(4’-methylbenzylidene)-1,3-indandione**



**Fig.2.16** **1H NMR spectrum of** **2-benzylidene-1,3-indandione**



**Fig.2.16** **1H NMR spectrum of** **2-benzylidene-1,3-indandione**



**Fig.2.17**  **1H NMR spectrum of** **2-(4’-chlorobenzylidene)-1,3-indandione**



**Fig.2.18**  **1H NMR spectrum of** **2-(4’-bromobenzylidene)-1,3-indandione**



**Fig.2.19**  **1H NMR spectrum of** **2-(4’-carboxybenzylidene)-1,3-indandione**

**2.2.4. Assignment of 13C NMR signals**

13C NMR signals were assigned for various carbons were based on the

1. Chemical shift exhibited by the signals.
2. Relative signal intensity.

13C chemical shifts were assigned by intensity and SCS consideration. 13C NMR spectra of substituted 2-benzylidene 1,3-indandiones are given in figure (2.20-2.25). the proton-noise decoupled spectrum of parent compound contains 14 signals corresponding to 14 different carbon atoms. In all the spectra, the two carbonyl carbon signals were readily recognized from their low intensity and also well separated from other signals to downfield extreme, since their assignment was not difficult.

One upfield signal was assigned for C7’ carbon atom at 135.45 ppm. The intensity was somewhat larger. The C6 carbon gives a peak at 135.25 ppm. The 13C chemical shifts of p-substituted 2-benzylidene 1.3-indandiones are given in Table (2.2).



**Fig.2.20** **13C NMR spectrum of** **2-(4’-methtoxybenzylidene)-1,3-indandione**



**Fig.2.21** **13C NMR spectrum of** **2-(4’-methylbenzylidene)-1,3-indandione**



**Fig.2.22**  **13C NMR spectrum of** **2-benzylidene-1,3-indandione**





**Fig.2.23**  **13C NMR spectrum of** **2-(4’-chlorobenzylidene)-1,3-indandione**



**Fig.2.24**  **13C NMR spectrum of** **2-(4’-bromobenzylidene)-1,3-indandione**



**Fig.2.25**  **13C NMR spectrum of** **2-(4’-carboxybenzylidene)-1,3-indandione**

Table (2.2): 13C NMR Chemical shifts of *p*- substituted 2-benzylidene -1,3-indandiones

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| S.No. | Substituent X | C1 | C3 | C6 | C7 | C1’ | C3’,5’ | C7 | C in  substituent |
| 1. | *p*-OCH3 | 190.86 | 189.54 | 134.87 | 123.07 | 126.46 | 114.38 | 146.86 | 55.60 |
| 2. | *p*-CH3 | 190.53 | 189.20 | 135.04 | 123.22 | 128.17 | 123.22 | 147.10 | 22.01 |
| 3. | H | 190.32 | 189.04 | 135.25 | 123.26 | 129.17 | 128.82 | 135.45 | - |
| 4. | *p*-Cl | 189.98 | 189.01 | 135.39 | 123.44 | 131.54 | 129.14 | 145.20 | - |
| 5. | *p*-Br | 189.96 | 189.01 | 135.57 | 123.44 | 129.63 | 132.16 | 145.27 | - |
| 6. | *p*-COOH | 189.34 | 188.60 | 136.36 | 123.64 | 134.37 | 129.70 | 144.36 | 39.05 |

**2.3 Preparation of *p*-substituted 5-benzylidenebarbituric acids**

5-benzylidenebarbituric acid and its substituted compounds were prepared by the modified procedure14.

To the calculated amount of the pure benzaldehyde (2 g, 0.015 mol) and barbituric acid (1.55g, 0.015 mol) in warm ethyl alcohol was added a 10% solution of sodium hydroxide (catalytic amount) and the reaction mixture stirred for 2 hours. After completion of the reaction as indicated by TLC, the reaction mixture was left overnight (scheme 2.2). The solvent was removed in vacuum. The resulting crude product was purified by column chromatography.



(Scheme 2.2)

**2.4 CHARACTERIZATION**

All the compounds were characterized as 5-benzylidenebarbituric acid and its derivatives (Fig.2.26) by 1H and 13C NMR spectral techniques. 1H and 13C spectra were obtained on a BRUKER AMX 400 MHz spectrometer. Chemical shift of 1H were measured with the peak of DMSO at δ 2.51 as the internal reference, while those of 13C were recorded with the central peak of DMSO at δ 39.90 as the internal reference.



Fig. (2.26)

**2.4.1 Assignment of 1H NMR Signals**

In 1H NMR spectrum of 5-benzylidenebarbituric acid whose, signals assignment was not difficult and all signals well separated from each other. The NH-proton of N8 and N10 atoms are expected to downfield than the -CH-proton of C5 carbon atom. The -CH-proton of C5 is well separated from all other protons signals, hence it’s assignment is not difficult. 1H NMR spectra of substituted 5-benzylidenebarbituric acids are given in Fig’s (2.27 – 2.33).

**1H NMR** Spectral data of substituted 5-benzylidenebarbituric acids are given below.

1. 5-(4’-Methoxybenzylidene)barbituric acid

**δ 3.877 (s,3H), 7.065 (d,2H), 8.252(s,1H), 8.369 (d,2H), 11.175 (s,1H), 11.302 (s,1H).**

2. 5-(4’-Hydroxybenzylidene)barbituric acid

**δ 6.878 (d,2H), 8.213 (s,1H), 8.320 (d,2H), 10.851 (s,1H), 11.117(s,1H), 11.249 (s,1H).**

3. 5-(4’-Methylbenzylidene)barbituric acid

**δ 2.385 (s,3H), 7.304 (d,2H), 8.094 (d,2H), 8.255 (s,1H), 11.218 (s,1H), 11.365 (s,1H).**

4. 5-Benzylidenebarbituric acid

**δ 7.485 (m,3H), 8.073 (d,2H), 8.285 (s,1H), 11.238 (s,1H), 11.397 (s,1H).**

5. 5-(4’-Chlorobenzylidene)barbituric acid

**δ 7.518 (d,2H), 8.069 (d,2H), 8.243 (s,1H), 11.275 (s,1H), 11.425 (s,1H).**

6. 5-(4’-Bromobenzylidene)barbituric acid

**δ 7.670 (d,2H), 7.979 (d,2H), 8.223 (s,1H), 11.272 (s,1H), 11.421 (s,1H).**

7. 5-(4’-Nitrobenzylidene)barbituric acid

**δ 8.017 (d,2H), 8.245 (d,2H), 8.324 (s,1H), 11.329 (s,1H), 1.504 (s,1H).**



**Fig.2.27 1H NMR spectrum of** **5-(4’-methoxybenzylidene)barbituric acid**



**Fig.2.28 1H NMR spectrum of** **5-(4’-hydroxybenzylidene)barbituric acid**



**Fig.2.29 1H NMR spectrum of** **5-(4’-methylbenzylidene)barbituric acid**

**Fig.2.30 1H NMR spectrum of** **5-benzylidenebarbituric acid**





**Fig.2.31 1H NMR spectrum of** **5-(4’-chlorobenzylidene)barbituric acid**



**Fig.2.32 1H NMR spectrum of** **5-(4’-bromobenzylidene)barbituric acid**



**Fig.2.33 1H NMR spectrum of** **5-(4’-nitroobenzylidene)barbituric acid**

**Table (2.3): 1H NMR chemical shifts of** **substituted 5-benzylidenebarbituric**

**acids**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  |  |  |
| S.No. | Substituent, -X |  | H22’ | H33’ | H5 | H8 | H10 |
|  |  |  |  |  |  |  |  |
| 1. | -OCH3 |  | 7.065 | 8.369 | 8.252 | 11.175 | 11.302 |
|  |  |  |  |  |  |  |  |
| 2. | -OH |  | 6.878 | 8.32 | 8.213 | 11.117 | 11.249 |
|  |  |  |  |  |  |  |  |
| 3. | -CH3 |  | 7.304 | 8.094 | 8.255 | 11.218 | 11.365 |
|  |  |  |  |  |  |  |  |
| 4. | -H |  | 7.485 | 8.073 | 8.285 | 11.238 | 11.397 |
|  |  |  |  |  |  |  |  |
| 5. | -Cl |  | 7.518 | 8.069 | 8.243 | 11.275 | 11.425 |
|  |  |  |  |  |  |  |  |
| 6. | -Br |  | 7.670 | 7.979 | 8.223 | 11.272 | 11.421 |
|  |  |  |  |  |  |  |  |
| 7. | -NO2 |  | 8.245 | 8.017 | 8.324 | 11.329 | 11.504 |

**2.4.2 Assignment of 13C NMR signals**

13C NMR signals were assigned for various carbons were based on the

1. Chemical shift exhibited by the signals
2. Relative signal intensity
3. Empirical additivity rules

13C NMR spectrum of 5-benzylidenebarbituric acid contains 9 signal corresponding to 9 different carbon atoms. In all the spectra, carbonyl carbon signal was readily recognized and also well separated from other signals to downfield extreme, since its assignment was not difficult. 13C NMR spectra of substituted

5-benzylidenebarbituric acids are given in fig’s (2.34 - 2.40).

**13C NMR Spectra of 5-benzylidenebarbituric acids**

1*.* 5-(4’-Methoxybenzylidene)barbituric acid

**δ 56.22, 114.41, 116.00, 125.62, 137.96, 150.67, 155.46, 162.64, 163.92, 164.39.**

2. 5-(4’-Hydroxybenzylidene)barbituric acid

**δ 114.61, 115.97, 124.24, 138.77, 150.70, 156.05, 162.75,163.48, 164.59.**

3. 5-(4’-Methylbenzylidene)barbituric acid

**δ 118.30, 129.33, 130.31, 134.43, 143.96, 150.68, 155.46, 162.26, 164.08.**

4. 5-Benzylidenebarbituric acid

**δ 119.55, 128.52, 132.69, 133.11, 133.54, 150.69, 155.20, 162.03, 163.87**.

5. 5-(4’-Chlorobenzylidene)barbituric acid

**δ 120.09, 128.55, 132.01, 135.15, 137.21, 150.65, 153.52, 162.04, 163.67.**

6. 5-(4’-Bromobenzylidene)barbituric acid

**δ 120.24, 126.29, 131.51, 132.40, 135.15, 150.65, 153.56, 162.04, 163.67.**

7. 5-(4’-Nitrobenzylidene)barbituric acid

**δ 123.15, 123.37, 132.69, 140.48, 148.49, 150.68, 151.63, 161.62, 163.13.**

****

**Fig.2.34 13C NMR spectrum of** **5-(4’-methoxybenzylidene)barbituric acid**

****

**Fig.2.35 13C NMR spectrum of** **5-(4’-hydroxybenzylidene)barbituric acid**

****

**Fig. 2.36 13C NMR spectrum of** **5-(4’-methylbenzylidene)barbituric acid**

****

**Fig.2.37 13C NMR spectrum of** **5-benzylidenebarbituric acid**

****

**Fig. 2.38 13C NMR spectrum of** **5-(4’-chlorobenzylidene)barbituric acid**

****

**Fig. 2.39 13C NMR spectrum of** **5-(4’-bromobenzylidene)barbituric acid**

****

**Fig.2.40 13C NMR spectrum of** **5-(4’-nitrobenzylidene)barbituric acid**

**Table (2.4): 13C NMR chemical shifts of substituted 5-benzylidenebarbituric acids**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No.** | *p*-X | **C1** | **C22’** | **C33’** | **C4** | **C5** | **C6** | **C7** | **C9** | **C11** |
|  |  |  |  |  |  |  |  |  |  |  |
| 1 | -OCH3 | 162.64 | 114.41 | 137.96 | 125.62 | 155.46 | 116 | 163.92 | 150.67 | 164.39 |
|  |  |  |  |  |  |  |  |  |  |  |
| 2 | -OH | 163.48 | 115.97 | 138.77 | 124.24 | 156.05 | 114.61 | 162.75 | 150.7 | 164.59 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3 | -CH3 | 143.96 | 129.33 | 134.43 | 130.31 | 155.46 | 118.3 | 162.26 | 150.68 | 164.08 |
|  |  |  |  |  |  |  |  |  |  |  |
| 4 | -H | 133.11 | 128.52 | 133.54 | 132.69 | 155.2 | 119.55 | 162.03 | 150.69 | 163.87 |
|  |  |  |  |  |  |  |  |  |  |  |
| 5 | -Cl | 137.21 | 128.55 | 135.15 | 132.01 | 153.52 | 120.09 | 162.04 | 150.65 | 163.67 |
|  |  |  |  |  |  |  |  |  |  |  |
| 6 | -Br | 126.29 | 131.51 | 135.15 | 132.4 | 153.56 | 120.24 | 162.04 | 150.65 | 163.67 |
|  |  |  |  |  |  |  |  |  |  |  |
| 7 | -NO2 | 148.49 | 132.69 | 123.37 | 140.48 | 151.63 | 123.15 | 161.62 | 150.68 | 163.13 |