

## Effect of the Substituents on the Infrared Absorptions of 2H-pyran-2-ones

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**Summary:** Infrared carbonyl and carbon-carbon double bond frequencies in appropriate solution, solid state and nujol are presented for a number of substituted 2H-pyran-2-ones. The effect of the substituents at the 3,4- and 4,6-positions on the carbonyl absorption frequencies of the 2H-pyran-2-one has been interpreted in terms of chemical effects. The influence of the amino group at the 3-position, p-methoxy phenyl at 4 or 4,6-positions and hydroxystyryl at the 6-position of the 2H-pyran-2-one has been found to lower the carbonyl absorption significantly as compared to the generally reported value of  $1700\text{ cm}^{-1}$  or above  $1700\text{ cm}^{-1}$ .

Infrared spectral data have been invaluable in the structure elucidation of virtually all classes of organic compounds. In the field of pyrones the previously reported investigations have been the studies of benzo-pyrone<sup>1,2</sup> system. The investigations of simple 2-pyrone derivatives without any fused aromatic ring have been carried out by Jones et. al<sup>3</sup>. with respect to the effect of solvent, temperature and concentration on carbonyl absorption. A partial investigation involving the effect of certain electrophilic substituent on the carbonyl absorption of the 2-pyrones was reported by Yamada<sup>4</sup>. Later studies<sup>5-7</sup> emphasise the existence of carbonyl absorptions above  $1700\text{ cm}^{-1}$  as the characteristic of 2H-pyran-2-one rings. However, no comprehensive account of the chemical effect of the substituents at the 3,4- and 4,6-positions of 2H-pyran-2-ones on the carbonyl absorptions have been reported.

In view of the synthetic importance and occurrence of 2-pyrone rings in the natural products,<sup>8</sup> a systematic study of the inductive or field effects of the substituents at the 3-position, the resonance interaction between the appropriate substituents at the 4 or 6-position on the carbonyl and carbon-carbon double bond stretching frequencies of a number of 2H-pyran-2-ones have been investigated and interpreted purely in qualitative terms. The absorption bands are susceptible to solvent and temperature effects<sup>3</sup> hence for comparison purposes the spectra (Tables - I, II) of the compounds of present study have been recorded in Nujol, solid (KBr) and solution forms at ambient temperature.

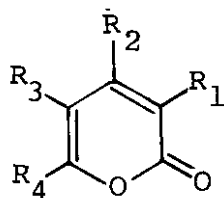
The characteristic absorption bands of simple 2H-pyran-2-ones have been reported<sup>3-7</sup> in the region  $1720-1750\text{ cm}^{-1}$  (CO of ring)  $1520-1650\text{ cm}^{-1}$

(-C=C-) and  $1210-1250\text{ cm}^{-1}$  (-C-O-C). The appearance of two bands in the carbonyl region of some pyrones has been interpreted in terms of Fermi effect<sup>3,9a</sup>. In table-I are listed carbonyl absorption bands of some substituted 2H-pyran-2-ones (VIII-XXI) having an electron withdrawing group at the 3-position. The higher  $\nu\text{CO}$  of pyrones (VIII-XII) as compared to the parent pyrone rings (III-VII) is explicable in terms of inductive effect or field effects of the substituents which lowers the polarity of the carbonyl bond and results in higher  $\nu\text{CO}$ . Analogous to the  $\alpha$ -haloesters,  $\alpha$ -haloketones<sup>9b</sup> and  $\alpha$ -halo- $\gamma$ -lactones<sup>10</sup> the presence of bromo-group in 2-pyrones (XIII-XVI) was expected to raise the frequency of the carbonyl absorption. On the contrary the 3-bromo-pyrones (XIII-XV) except (XVI) exhibited a slight negative deviation as compared to the parent pyrones (II-IV). Discrepancies similar to this have been observed<sup>9b</sup> in  $\alpha$ -polyhalogenated aldehydes and  $\alpha$ -nitroacetophenone and explained on the basis of field effect<sup>11</sup> rather the inductive effect. Presumably, in the bromopyrones (XIII-XV) also, the bromine atom is not suitably oriented to produce the desired field effect.

3,3-Bis-pyrone sulphide (XVII, XVIII) show a carbonyl absorption appreciably lower than the parent pyrones (III, VI) in Nujol, while in solution and solid the effect is negligible. This is presumably due to the interaction between the sulphur and oxygen of the carbonyl group through the field effect. The sulphur atoms situated in close proximity of the carbonyl groups in aldehydes have also been reported<sup>9c</sup> to exhibit analogous behaviour.

The spectral data in solution pertaining to carbonyl absorption of the 3-acetyl-4-alkoxy-2-pyrone

Table 1. Infrared carbonyl absorption bands of substituted 2H-pyran-2-ones.



Compounds	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Nujol	KBr	CHCl <sub>3</sub>
*I	H	H	H	H		1736	1739 1721
II	H	Me	H	Me	1725 1705	1736 1703	1725 1706
III	H	OH	H	Me	1719	1720	1724
IV	H	Ph	Ph	Ph	1725	1721	1725
V	H	OH	H	Ph	1695	1705	1710
VI	H	OMe	H	Me	1736 1706	1705	1709
VII	H	OCH <sub>2</sub> Ph	H	Me	1725	1710	1715
VIII	NO <sub>2</sub>	OMe	H	Me	1720	1720	1725
IX	NO <sub>2</sub>	Ph	Ph	Ph	1745	1740	1750
X	NO <sub>2</sub>	OH	H	Me	1760	1750	1755
XI	NO <sub>2</sub>	OH	H	P.NO <sub>2</sub> . Ph	1745	1745	1753
XII	N-N. Ph	OH	H	Me	1735	1725	1733
XIII	Br	OH	H	Me	1720	1705	1720
XIV	Br	Me	H	Me	1715	1712	1715
XV	Br	Ph	Ph	Ph	1720	1715	1718
XVI	Br	OMe	H	Me	1735	1720	1720
XVII	-S-bis	OH	H	Me	1700	1705	1710
XVIII	-S-bis	OMe	H	Me	1720	1705	1708
XIX	MeCO	OMe	H	Me	1720	1718	1720
XX	MeCO	OEt	H	Me	1720	1718	1725
XXI	MeCO	OCH <sub>2</sub> Ph	H	Me	1720	1718	1725
XXII	NH <sub>2</sub>	OMe	H	Me	1680	1683	1686
XXIII	NH <sub>2</sub>	OH	H	Me	1680	1680	1682
XXIV	NHCOMe	OH	H	Me	1680	1680	1685
XXV	H	MeCO <sub>2</sub>	H	Me	1739	1734	1735
XXVI	H	(Me) <sub>2</sub> CO <sub>2</sub>	H	Me	1730	1728	1725

Table 1 (Continued)

Compounds	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Nujol	KBr	CHCl <sub>3</sub>
XXVII	H	MeCO <sub>2</sub>	H	Ph	1715	1710	1712
XXVIII	H	C <sub>4</sub> H <sub>8</sub> N	H	Me	1690	1683	1685
XXIX	H	C <sub>5</sub> H <sub>10</sub> N	H	Me	1680	1680	1680
XXX	H	(Me) <sub>2</sub> N	H	Me	1690	1685	1685
XXXI	H	Ph	H	Ph	1705	1702W	1705W
XXXII	H	OMe	H	Ph	1705	1706S	1706S
XXXIII	H	p-MeOPh	H	Ph	1685	1688W	1690S
XXXIV	H	p-MeOPh	H	p-MeOPh	1690	1690W	1695W
XXXV	H	OMe	H	styryl	1720	1720	1720
XXXVI	H	OMe	H	4-MeO-styryl	1724	1723	1724
XXXVII	H	OMe	H	3-MeO-styryl	1725	1724	1724
XXXVIII	H	OMe	H	3,4-di-MeO-styryl	1710	1701	1705
XXXix	H	OMe	H	4-OH-styryl	1700	1690	1700
XXXX	H	OMe	H	3-OH-styryl	1670	1665	1668
XXXXI	H	OMe	H	3,4-di, OH-styryl	1675	1668	1672
XXXXII	H	OH	H	styryl	1725	1720	1725
XXXXIII	H	OH	H	4-OH-styryl	1690	1685	1688
XXXXIV	H	OH	H	3-OH-styryl	1695	1690	1690
XXXXV	H	OH	H	3,4-di,OH-styryl	1690	1683	1690

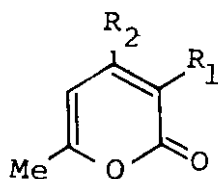
\*Data taken from ref.-3.

(XIX-XXI) show a slight rise in their  $\nu$ CO as compared to 4-methoxy-2-pyrone (VI). This is probably due to the electron withdrawing effect of the acetyl group which runs counter to the conjugative effect of the alkoxy group.

Comparison of carbonyl absorption data of 3-amino derivative (XXII-XXIV) indicates that the introduction of the 3-amino group into the 2-pyrone (III-VI) causes a downward shift of 30-40  $\text{cm}^{-1}$ . These large shifts probably are indicative of strong hydrogen bonding. An effect of the same magnitude has also been reported<sup>9d,12</sup> for o-aminoacetophenone as compared to acetophenone. The spectral data of 2-pyrones (II, VI, VII, XXV-XXX) having an electron donating substituent at the 4-position show a significant lowering of  $\nu$ CO. However the intensity

of the effect depends upon the nature of the substituents. The presence of a methyl group at 4-position lowers the  $\nu$ CO to a smaller extent e.g. the solution spectra of (I) and (II) show  $\nu$ CO at 1739  $\text{cm}^{-1}$  and 1725  $\text{cm}^{-1}$  respectively. The impact of the substituent with an atom carrying a suitably oriented lone pair which can delocalise with the carbonyl of the ring, has been found to be significant. The solution spectra of the 4-alkoxy-2-pyrone (VI-VII) and 4-acyloxy-2-pyrone (XXV-XXVII) show  $\nu$ CO at 1709  $\text{cm}^{-1}$  and 1715-1730  $\text{cm}^{-1}$  respectively as compared to the 2-pyrone (I, CO=1739  $\text{cm}^{-1}$ ). The carbonyl absorptions of 4-secondary amino-2-pyrones (XXVII-XXX) at 1680-1685  $\text{cm}^{-1}$  are of considerable interest, where the resonance interaction between the lone pair of nitrogen of the substituent at the 4-

Table II. Infrared Carbon-Carbon double bond Absorption bands of substituted 2H-pyran-2-ones.



Compound	R <sub>1</sub>	R <sub>2</sub>	Nujol	KBr	CHCl <sub>3</sub>
II	H	Me	1645, 1575	1640, 1575	1640, 1570
III	H	OH	1630, 1594	1650, 1590	1650, 1578
X	NO <sub>2</sub>	OH	1650, 1550	1650, 1525	1640, 1525
XII	N=N. Ph	OH	1655, 1585	1650, 1585	1655, 1580
XIII	Br	OH	1661, 1580	1650, 1580	1650, 1565
XVII	-S-bis	OH	1655, 1510	1645, 1515	1645, 1510
XXIII	NH <sub>2</sub>	OH	1650, 1535	1650, 1530	1650, 1535
XXIV	NHCOMe	OH	1660, 1570	1655, 1570	1660, 1560
VI	H	OMe	1680, 1575	1680, 1570	1680, 1575
VIII	NO <sub>2</sub>	OMe	1620, 1550	1620, 1550	1615, 1545
XVIII	-S-bis	OMe	1648, 1555	1648, 1550	1648, 1555
XVI	Br	OMe	1660, 1525	1662, 1530	1640, 1525
XIX	COMe	OMe	1615, 1548	1625, 1545	1615, 1545
XX	COMe	OMe	1615, 1545	1620, 1548	1620, 1548
XXVIII	H	C <sub>4</sub> H <sub>8</sub> N	1645, 1560	1645, 1555	1650, 1545
XXIX	H	C <sub>5</sub> H <sub>10</sub> N	1650, 1550	1645, 1550	1650, 1550
XXX	H	(Me) <sub>2</sub> N	1650, 1546	1650, 1545	1655, 1545

position and the carbonyl of the ring appears to be a maximum giving the subsequent lowering of carbonyl absorptions by 54-59 cm<sup>-1</sup> as compared to the 2-pyrone (I). In general the lowering of the carbonyl absorption by the substituent at the 4-position has been found out to be in the order of secondary amino > methoxy > methyl > acyloxy.

The  $\nu_{\text{CO}}$  (KBr) of 4-6-diphenyl-2-pyrone (XXXI), 4-methoxy-6-phenyl-2-pyrone (XXXII) and 4,5,6-triphenyl-2-pyrone (IV) appear at 1702 cm<sup>-1</sup>, 1706 cm<sup>-1</sup> and 1721 cm<sup>-1</sup> respectively. This downward shift of  $\nu_{\text{CO}}$  as compared to (I,II) is explicable in terms of conjugative effect of the phenyl substitu-

ents. The effect appears to be maximum when the phenyl substituents are at the 4- and 6-positions, J.H. Looker<sup>13</sup> et. al. have reported the non existence of any significant resonance interaction between the appropriately placed methoxy group in the benzene ring and the carbonyl of pyrone in the monomethoxy flavone molecule. On the contrary here it has been observed that the presence of p-methoxyphenyl substituent at the 4- or 4,6-positions exerts a strong influence as evident from  $\nu_{\text{CO}}$  of (XXXIII) and (XXXIV) at 1688 cm<sup>-1</sup> and 1690 cm<sup>-1</sup> respectively. The effect of the same magnitude has also been observed by Hergert et al.<sup>1</sup> on the  $\nu_{\text{CO}}$  of ortho or para-methoxy acetophenone.

The solution infrared carbonyl absorption data pertaining to the 6-styryl derivative (XXXV-XXXV) presents an unusual effect of the substituents. The compounds (XXXV-XXXVIII) showed carbonyl absorption in the region 1700-1724. However, the presence of hydroxyl group at the 3- or 4- 3,4-positions of the phenyl ring in compound (XXXIX), (XXXX) and (XXXI) showed the  $\nu_{\text{CO}}$  at 1700, 1668 and 1672  $\text{cm}^{-1}$  respectively. A negative shift of lesser magnitude was observed in compounds (XXXII-XXXXV) where the hydroxyl groups were present at the 3 or 4- or 3,4-positions of the styryl part and at the 4-position of 2-pyrone. These observations are in good agreement with the values quoted by other workers<sup>14</sup> in solid state spectra. The negative deviation of  $\nu_{\text{CO}}$ , especially in compounds (XXXXIX-XXXI) is attributable to the conjugative effect of 6-(hydroxy-styryl and 4-methoxy group alongwith intermolecular hydrogen bonding.

From these results, it may be concluded that the general criteria for the characterisation of 2H-pyran-2-ones on the basis of carbonyl absorption (i.e. above 1700  $\text{cm}^{-1}$ ) alone must be used with caution especially when the amino group at the 3-position, secondary amino group at the 4-position, p-methoxyphenyl at the 4 or 4,6-positions and hydroxystyryl at the 6-position are present as the substituents.

In addition to the carbonyl absorption, the two bands in the region 1560-1567  $\text{cm}^{-1}$  and 1634-1647  $\text{cm}^{-1}$  associated with the asymmetric and symmetric stretching of the carbon-carbon double bond have been reported to be the characteristic of 2H-pyran-2-one rings. The stretching frequencies of some pyrone derivatives without the phenyl substituents in the region 1500-1680  $\text{cm}^{-1}$  are summarised in the table-II.

The bands at higher frequencies in the 3-substituted-4-hydroxy-2-pyrones (III, X, XII, XIII, XVII, XXIII, XXIV) appear consistently in the region 1640-1660  $\text{cm}^{-1}$  thus showing an insignificant effect of the substituents. However, the only noticeable effect of substituents has been the increased intensities of these band in the 3-substituted products as compared to the parent 4-hydroxy-2-pyrone (III). On the contrary the lower bands (1500-1600  $\text{cm}^{-1}$ ) are deeply influenced and appear in the region 1510-1580  $\text{cm}^{-1}$  as compared to the original band at 1578  $\text{cm}^{-1}$ . An analogous effect has also been observed in the 3-substituted-4-methoxy-2-pyrones (VI, VIII, XVIII, XVI) and 3-secondary amino-

2-pyrones (XXVIII-XXX). The absorption of 3-acyl derivative (XIX, XX) and 3-nitro derivative (VIII) is an exception, where both the bands are lowered to 1615-1620  $\text{cm}^{-1}$  and 1545-1548 as compared to original bands at 1680  $\text{cm}^{-1}$ , 1575  $\text{cm}^{-1}$  in the parent ring (VI). From these observations, it appears difficult to rationalise in unequivocal terms the influence of the substituents on the carbon-carbon double bond on the basis of the chemical effect without additional extensive experimentation.

## Experimental

The spectra were measured with Perkin-Elmer SP 200 and JASCO-IRA-1 spectrophotometers. Solution spectra ( $\text{CHCl}_3$ ) were determined on either saturated or dilute solution depending upon the solubility of the compound. A matched cell containing pure solvent was employed in balancing the beam to correct for solvent absorption. Solid state potassium bromide disc spectra were determined with several thickness of disk as necessary to make the typical bands sufficiently intense. All carbonyl absorptions were corrected as necessary by reference to the 1601.4  $\text{cm}^{-1}$  bands of polystyrene.

The following compounds used in the present investigation were prepared by the methods as given in literature. (II) m.p. 48°C (lit.<sup>15</sup> m.p. 49-50°C); (III) m.p. 187-189°C (lit.<sup>16</sup> m.p. 189°C); (IV) m.p. 155°C (lit.<sup>17</sup> m.p. 158°C); (V) m.p. 245°C (lit.<sup>18</sup> m.p. 245°C); (VI) m.p. 87°C (lit.<sup>7,19</sup> m.p. 87.5-88°C); (VIII) m.p. 168°C (lit.<sup>4,19</sup> m.p. 165-167°C); (IX) m.p. 170°C (lit.<sup>20</sup> m.p. 171°C). (X) m.p. 165°C (lit.<sup>4,19</sup> m.p. 162-165°C); (XII) m.p. 192-193°C (lit.<sup>21</sup> m.p. 192-193°C); (XIII) m.p. 210°C (lit.<sup>4,19</sup> m.p. 210°C). (XIV) m.p. 101-102°C (lit.<sup>22</sup> m.p. 102-104°C); (XV) m.p. 180°C (lit.<sup>20</sup> m.p. 178°C); (XVI) m.p. 153°C (lit.<sup>4,19</sup> m.p. 155°C); (XVII) m.p. 260°C (lit.<sup>21</sup> m.p. 260°C); (XVIII) m.p. 190°C (lit.<sup>21</sup> m.p. 190°C); (XIX) m.p. 93°C (lit.<sup>23</sup> m.p. 91°C); (XX) m.p. 92°C (lit.<sup>24</sup> m.p. 93.95°C); (XXII) m.p. 115°C (lit.<sup>21</sup> m.p. 115°C); (XXIII) m.p. 140°C (lit.<sup>21</sup> m.p. 140°C). (XXIV) m.p. 192°C (lit.<sup>25</sup> m.p. 191-195°C); (XXV) m.p. 42-45°C (lit.<sup>26</sup> m.p. 42-45°C); (XXVI) m.p. 33-34°C (lit.<sup>26</sup> m.p. 34-36°C); (XXVII) m.p. 80-82°C (lit.<sup>26</sup> m.p. 79-83°C); (XXVIII) m.p. 180°C (lit.<sup>27</sup> m.p. 180°C);

(XXIX) m.p. 170°C (lit.<sup>27</sup> m.p. 170°C); (XXX) m.p. 150°C (lit.<sup>27</sup> m.p. 150°C); (XXXI) m.p. 140°C (lit.<sup>28</sup> m.p. 140°C); (XXXIII) m.p. 145°C (lit.<sup>28</sup> m.p. 147°C); (XXXIV) m.p. 175°C (lit.<sup>28</sup> m.p. 174°C).

#### 4-benzyloxy-6-methyl-2H-pyran-2-one (VII)

A mixture of 4-hydroxy-6-methyl-2H-pyran-2-one (III, 5g.), benzylchloride (10g.) and potassium carbonate (20g.) in ethyl methyl ketone (120 ml) was refluxed with stirring for 48 hrs. After cooling the reaction mixture was filtered. The filtrate on evaporation gave a liquid residue which on refrigeration and addition of cyclohexane afforded white solid. Crystallisation from benzene-cyclohexane mixture (1:2) gave shining needles m.p. 92°C.  $\nu_{\max}$ . 1730, 1650, 1850  $\text{cm}^{-1}$   $\lambda_{\max}$ . (EtOH). 281 nm (log  $\epsilon$  3.75) nmr (CDCl<sub>3</sub>) 2.2 (3H), 5.0 (2H), 5.5 (1H), 5.85 (1H), 7.4 (5H) aromatic; (Found: C, 72.08, H, 5.45, C<sub>13</sub>H<sub>12</sub>O<sub>3</sub> requires C, 72.22; H, 5.55%) mass spectrum m/e 216 M<sup>+</sup>

#### 4-hydroxy-3-Nitro-6-p-nitrophenyl-2H-pyran-2-one (XI)

4-hydroxy-6-phenyl-2H-pyran-2-one ( $\nu$ , 2g). was dissolved in concentrated sulphuric acid 98% (10.0 ml) and solution was cooled to 0°C. Nitrating mixture (concentrated sulphuric acid 8ml and concentrated nitric acid 2.0 ml) was added dropwise maintaining the temperature below 10°C. The reaction mixture was poured onto crushed ice. A brownish yellow sticky mass was obtained which on crystallisation from ethanol-chloroform (4:1) mixture gave light brown microcrystalline solid m.p. 201°C (Dec).  $\nu_{\max}$ . 1740, 1720, 1630, 1650; nmr (DMSO) 2.5 (DMSO Protons), 7.0 (1H), 7.6 (1H enolic, 8.2-8.7 (4H aromatic). (Found: C, 47.63; H, 2.43; N, 9.75, C<sub>11</sub>H<sub>6</sub>N<sub>2</sub>O<sub>7</sub> requires C, 47.48; H, 2.15; N, 10.07%).

#### 3-Acetyl-4-benzyloxy-6-methyl-2H-pyran-2-one (XXI).

A mixture of silver salt of dehydroacetic acid (5g.), benzylchloride (4.3g.) and methyl cyanide (10 ml) was refluxed for 2.5 hours. after the removal of liquid portion under reduced pressure the residue was extracted with hot ethanol (50 ml). The ethanolic extract on evaporation under reduced pressure gave a semi-solid mass which on crystallisation from ether-petroleum ether (60-80°C) mixture gave white

shining needles m.p. 94-95°C gmax. 1720, 1660, 1540  $\text{cm}^{-1}$ ;  $\lambda_{\max}$ . (EtOH) 313 nm (log  $\epsilon$  3.69), 226 nm (log  $\epsilon$  3.81); nmr (CDCl<sub>3</sub>) 2.28 (3H), 5.2 (2H), 6.1 (1H), 7.36 (5H, aromatic); (Found: C, 69.95; H, 5.52, C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>, requires C, 69.76; H, 5.43%); mass spectrum m/e 258 (M<sup>+</sup>).

#### 4-Methoxy-6-phenyl-2H-pyran-2-one (XXXII)

A mixture of 4-hydroxy-6-phenyl-2H-pyran-2-one (V, 1. Og.), dimethylsulphate (1 ml) and anhydrous potassium carbonate (4g.) in acetone (20 ml) was refluxed with stirring for 15 hours. The reaction mixture was then filtered. Filtrate on evaporation gave a viscous residue which on crystallisation from cyclohexane afforded light yellow solid m.p. 128-130°C lit.<sup>5c</sup> m.p. 129.5-131.5°C  $\nu_{\max}$ . (CHCl<sub>3</sub>) 1706  $\text{cm}^{-1}$ ;  $\lambda_{\max}$ . (EtOH). 315 nm (log  $\epsilon$  4.12.). (Found: C, 71.4; H, 4.9; C<sub>12</sub>H<sub>10</sub>O<sub>3</sub> requires C, 71.28; H, 4.95%).

#### 6-(methoxystyryl)-4-methoxy-2H-pyran-2-ones (XXXV-XXXVII)

A mixture of appropriate aldehyde or methoxy-aldehyde (0.02 M), 4-methoxy-6-methyl-2H-pyran-2-one (V, 0.02 M) and magnesium methoxide (1.5g. magnesium in 50 ml methanol) was refluxed for 4-6 hours. After the removal of solvent, the viscous residue was treated with ice cold dilute hydrochloric acid (5-10°C) and then extracted with chloroform. Extracts were washed with water, dried over magnesium sulphate and evaporated. The yellow oily products on trituration with ether gave compounds (XXXV) m.p. 138°C (lit.<sup>29</sup> m.p. 139-140°C); (XXXVI) m.p. 154°C (lit.<sup>7</sup> m.p. 155-157°C), (XXXVII) m.p. 135°C (lit.<sup>14</sup> m.p. 137°C), (XXXVIII) m.p. 160-162°C (lit.<sup>14</sup> m.p. 164°C). 6-(Hydroxystyryl)-4-methoxy-2H-pyran-2-ones (XXXIX) m.p. 277°C, (XXXX) m.p. 210°C, (XXXXI) m.p. 255°C and 6-(hydroxystyryl)-4-hydroxy-2H-pyran-2-ones (XXXXIII) m.p. 251-253°C, (XXXXIV) m.p. 185-190°C and (XXXXV) m.p. 255-258°C were prepared by the method of Edward and Mir<sup>14</sup>

#### 6-Styryl-4-hydroxy-2H-pyran-2-one (XXXXII)

6-Styryl-4-methoxy-2H-pyran-2-one (XXXV) (lg.) was heated with acetic acid-hydromic acid mixture

(3:1) 15 ml on a steam bath for 15 minutes. After cooling the reaction mixture was poured into ice-water mixture. The mixture was neutralized with sodium carbonate to pH 5. The resulting solid product was filtered and washed with water m.p. 245°C (lit.<sup>30</sup> m.p. 245-246°C).

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