Synthesis and Studies of some Substituted Naphthalides

E. SINGH and P. C. GUPTA

Chemistry Department, Allahabad University, Allahabad, India

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A number of naphthalides in which the central carbon (C*) atom is attached to different rings obtained by condensation of phenols with 3-benzoyl-2-naphthoic acid are described. The constitution of the dyes has been studied and the visible UV and IR spectra have been presented and discussed. The absorption maxima of the dyes have been found to be shifted like those of phthalicn.

The γ-keto acids (I) (substituted or unsubstituted) have been found to cyclic to their γ-hydroxy lactones (II) which yield well crystalline acetyl derivatives retaining their cyclic structures. Acetyl derivatives (III), esters and alkyl derivatives of phthalaldehydeic acid (IV; R = H) are ring tautomers. Levulinic (β-acetyl propionic acid) and β-benzoyl propionic acids yield well crystalline acetyl derivatives. Levulinic acid has further been shown to be a mixture of ring and chain tautomers.

The cyclic derivatives, pseudo chloride and pseudo esters are obtained through lactol intermediate. IR, Raman spectra and nmr spectra has further confirmed the formation of the iso.

The acid chloride from 8-benzoyl-1-naphthoic acid, which was purified by repeated crystallisation from rectified benzene and distilled acetone, was used. The benzylic esters of benzoyl-1-naphthoic acid is 56% - 65% when used.

The light yellow dye is microcrystalline, mp 226 - 228°. The ethanolic solution is light orange red (light green fluorescent) which on addition of alkali changes to bright red colour with intensified fluorescence. The absorption maxima (UV and visible) have been recorded using model DU Beckman Spectrophotometer in absolute ethanol (neutral and alkaline media) and IR were determined from KBr using a Perkin Elmer infracord.

The phenols (phenol, resorcinol, catechol, quinol, phloroglucinol and pyrogallol) have been taken in slight excess of molecular proportion than the acid (IV). Concentrated H₂SO₄ (4 — 6 drops) has been used as condensing agent throughout and each dye, when tested, is found free from sulphur.

The preparation of the rest of the dyes, shown in Table I, has been done in identical manner as already described (yield 56 — 65%).

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Anal. for C₆H₄O₄:
Calc.: C 78.26 H 4.35, M wt 368.00,
Found: C 78.27 H 4.19, M wt 355.00 (Rast).

The preparation of the rest of the dyes, shown in Table I, has been done in identical manner as already described (yield 56 — 65%).

Chromatography of dye (VII a): On test paper — Whatman No. 1, n-butanol-ammonia was allowed to run for 13 hrs. (descending) to give a single pink spot of the dye (VII a) showing the purity of the compound.

Acetylation of dye (VII b): The dye (0.5 g), acetic anhydride (10 ml) and fused sodium acetate (1.0 g) were refluxed at 130 — 140° for 4 hrs. to give a light yellow crystalline compound (0.5 g), mp 182° (from
Results and Discussion

Different substituted naphthalides (VII) have been prepared by the condensation of acid (IV) with phenols (VI). The condensation of phenols follows through the equilibrium process of lactol (V) of the acid (IV) and with excess of phenol the entire acid taken reacts as lactol. Analogous to phthalines in case of phenol the condensation may have been prepared by the condensation of acid (IV) with phenols (VI). The condensation of phenols follows through the equilibrium process of lactol (V) of the acid (IV) and with excess of phenol the entire acid taken reacts as lactol. Analogous to phthalines in case of phenol the condensation may have been prepared by the condensation of acid (IV) with phenols (VI). The condensation of phenols follows through the equilibrium process of lactol (V) of the acid (IV) and with excess of phenol the entire acid taken reacts as lactol. Analogous to phthalines in case of phenol the condensation may
take place at ortho\textsuperscript{23} or para-position\textsuperscript{24} or at both positions\textsuperscript{25}. Owing to small amount of the compound this has not been proved.

The purity of the dye (VII a) has been confirmed by paper chromatography. The structure has been confirmed by chemical and i.r. studies (3300 cm\textsuperscript{-1}, -OH and 1760 cm\textsuperscript{-1}, \(\gamma\)-lactone). Potassium hydroxide fusion of the dye (VII b) produced (IV) and resorcinol (VIII). The diacetyl derivative (VII g) and dibromo derivative (VII h) support the presence of resorcinol moiety in the dye (VII b). The compounds (VII b–VII h) posses \(\gamma\)-lactone (1765 cm\textsuperscript{-1}). The peak at 3350 cm\textsuperscript{-1} (OH) in (VII b) has been found to be absent in (VII g) and new peaks at 1200 and 1125 cm\textsuperscript{-1} (phenolic acetate) appear.

The absorption maxima (\(\lambda_{\text{max}}\)) of these substituted naphthalides (VII) given in Table 2 have been found to be in good agreement with those of known true phthaleins prepared in similar manner (Table 3).

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<table>
<thead>
<tr>
<th>Dyes</th>
<th>Colour in Absolute ethanol</th>
<th>Alkaline (absolute ethanol + 1 drop of 2% NaOH)</th>
<th>Colour with 2% NaOH</th>
<th>EtOH (\lambda_{\text{max}})</th>
<th>EtOH — NaOH (\lambda_{\text{max}})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII a</td>
<td>colour-less</td>
<td>reddish pink</td>
<td>dark pink</td>
<td>—</td>
<td>560</td>
<td>10.8</td>
</tr>
<tr>
<td>VII b</td>
<td>light orange</td>
<td>beautiful red (G. F.)</td>
<td>reddish pink</td>
<td>495</td>
<td>510</td>
<td>9.8</td>
</tr>
<tr>
<td>VII c</td>
<td>colour-less</td>
<td>orange-pink red</td>
<td>dark red</td>
<td>480</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>VII d</td>
<td>yellow brown</td>
<td>dark yellow brown</td>
<td>greenish brown changing to brownish red</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>VII e</td>
<td>light Yellow-red</td>
<td>reddish pink</td>
<td>pink</td>
<td>440</td>
<td>500</td>
<td>9.7</td>
</tr>
<tr>
<td>VII f</td>
<td>yellow red</td>
<td>dull red</td>
<td>brownish red</td>
<td>470</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>VII g</td>
<td>faint yellow</td>
<td>faint yellow</td>
<td>faint yellow</td>
<td>330</td>
<td>330</td>
<td>7.9</td>
</tr>
<tr>
<td>VII h</td>
<td>light pink (G. F.)</td>
<td>orange pink (G. F.)</td>
<td>pinkish red</td>
<td>530</td>
<td>520</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Table 2. Absorption maxima (\(\mu\mu\)) of substituted naphthalides (VII). G.F. = Green fluorescence.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Colour in Neuteral</th>
<th>Colour with 2% NaOH</th>
<th>EtOH (\lambda_{\text{max}})</th>
<th>EtOH — NaOH (\lambda_{\text{max}})</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolphthalein</td>
<td>colour-less</td>
<td>pink</td>
<td>pink</td>
<td>—</td>
<td>550</td>
</tr>
<tr>
<td>Fluorescein</td>
<td>yellow red</td>
<td>red (G. F.)</td>
<td>reddish pink (G. F.)</td>
<td>480</td>
<td>500</td>
</tr>
<tr>
<td>Eosin</td>
<td>light pink (G. F.)</td>
<td>orange pink (G. F.)</td>
<td>pink</td>
<td>530</td>
<td>530</td>
</tr>
</tbody>
</table>

Table 3. Absorption maxima (\(\mu\mu\)) of known phthaleins.
3. P. R. Jones and S. L. Congdon, J. Amer. chem. Soc. 81, 4291 [1959].
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