DERIVATIVES OF 1-HYDROXY-2-NAPHTHOIC ACID.

Part IV. Compounds Derived from 4-Nitro-1-hydroxy-2-naphthoic Acid and Its Methyl Ether.

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In continuation of the previous work, the nitration of methyl 1-hydroxy-2-naphthoate and its methyl ether has now been studied. Direct nitration of the hydroxy acid gives mostly 2:4-dinitro-1-naphthol; the direct nitration of the methoxy acid can be effected, however, at low temperature. The hydroxy acid was nitrated by König through intermediate sulphonation. The nitro-group in both the cases was found to enter in the 4-position. The nitration of the methyl esters is smooth and convenient. Methyl 1-hydroxy-2-naphthoate has been nitrated by Einhorn and Pfyl, who, however, did not study its constitution.

The acids obtained from the nitrated esters yielded the respective naphthoyl chlorides with phosphorus pentachloride. Various derivatives of these acids have been prepared from the naphthoyl chlorides.

The work is being extended.

Experimental.

Methyl 4-nitro-1-hydroxy-2-naphthoate.—Nitric acid (d. 1.42; 5 c.c.) in acetic acid (10 c.c.) was slowly added at room temperature to methyl 1-hydroxy-2-naphthoate (12 g.) in acetic acid (120 c.c.). The nitro-ester separated in yellow needles. The resultant mixture was diluted with water and filtered (14 g.). Pale yellow needles from acetic acid; m.p. 159-60° (161°, Einhorn and Pfyl, loc. cit.).

[Found: N (micro), 5.7; C₁₂H₉O₅N requires N, 5.7 per cent.]

4-Nitro-1-hydroxy-2-naphthoic acid.—The above ester (10 g.) was heated with alcoholic sodium hydroxide (100 c.c.; 2 N; rectified spirit 30 c.c.) for two
hours on the water-bath. The acid obtained on acidification (7 g.) crystal-
lised from acetic acid in thick pale yellow needles, m.p. 212-14° (decom.)
(212°, Konig, loc. cit.).

[Found : N (micro), 5·9; C₁₁H₄O₅N requires N, 6·0 per cent.]

2∶4-dinitro-1-naphthol, m.p. 138-39°, was obtained on heating the acid
(1 g.) in acetic acid (15 c.c.) with nitric acid (d. 1·42; 2 c.c.) in acetic acid
(4 c.c.); the mixed m.p. with an authentic sample showed no depression.

4-Nitro-1-hydroxy-2-naphthoyl chloride.—The clear solution obtained on
heating a mixture of the nitro-acid (2 g.), phosphorus pentachloride (4 g.)
and dry benzene (6 c.c.) on the water-bath, was filtered and dry petroleum
ether (10 c.c.) was added to the filtrate. The naphthoyl chloride which
slowly separated in yellow needles was filtered and dried over phosphorus
pentoxide under reduced pressure, m.p. 132-33°.

[Found : Cl, 14·1; C₁₁H₄O₅NCl requires Cl, 14·1 per cent.]

Methyl 4-nitro-1-methoxy-2-naphthoate.—Solutions of methyl 1-methoxy-
2-naphthoate from methyl 1-hydroxy-2-naphthoate (20 g.) in acetic acid
(solution made up to 80 c.c.) and nitric acid (d. 1·42; 8 c.c.) in acetic acid
(8 c.c.) were mixed and heated on the water-bath for fifteen minutes. The
nitro-ester (14 g.) separated on cooling and crystallised from methyl alcohol
in pale yellow needles, m.p. 110-11°.

[Found : N (micro), 5·5; C₁₃H₁₀O₅N requires N, 5·4 per cent.]

4-Nitro-1-methoxy-2-naphthoic acid.—The above ester (14 g.) was heated
on the water-bath with alcoholic sodium hydroxide (60 c.c. 2 N; rectified
spirit 100 c.c.) for half an hour. The acid (8 g.) obtained on acidification
crystallised from rectified spirit in pale yellow needles, m.p. 196-97°.
(195-96°, Froelicher and Cohen, loc. cit.)

[Found : N, 5·8; C₁₃H₉O₅N requires N, 5·7 per cent.]

4-Nitro-1-hydroxy-2-naphthoic acid (confirmed by mixed m.p.) was
obtained, when the methoxy acid (1 g.) in acetic acid (5 c.c.) was heated
with hydriodic acid (d. 1·5; 6 c.c.) for 10 minutes. The mixture was kept
overnight and the solid obtained on dilution crystallised from acetic acid
in thick pale yellow needles, m.p. 212-14° (decom.).

4-Nitro-1-methoxy-2-naphthoyl chloride.—The clear solution obtained on
heating, on the water-bath, a mixture of the nitro acid (2 g.), phosphorus
pentachloride (2 g.) and dry benzene (6 c.c.) was filtered and treated with
dry petroleum ether (25 c.c.). The naphthoyl chloride which slowly separated

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### Derivatives of 1-Hydroxy-2-Naphthoic Acid

<table>
<thead>
<tr>
<th>M.P.</th>
<th>Appearance</th>
<th>Solvent</th>
<th>Nitrogen analysis (micro)</th>
<th>Required Nitrogen (micro)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-60°</td>
<td>Thick pale yellow needles</td>
<td>Acetic acid</td>
<td>4.5 per cent.</td>
<td>4.6</td>
</tr>
<tr>
<td>103-4°</td>
<td>Flat pale yellow needles</td>
<td>Rectified spirit</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>231-2° (decom.)</td>
<td>Silky needles</td>
<td>Acetic acid</td>
<td>9.1</td>
<td>9.2</td>
</tr>
<tr>
<td>201-2° (decom.)</td>
<td>Thick pale yellow needles</td>
<td>Rectified spirit</td>
<td>8.7</td>
<td>8.7</td>
</tr>
<tr>
<td>236-37°</td>
<td>Silky pale yellow needles</td>
<td>Acetic acid</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>258-9°</td>
<td>Thick pale yellow needles</td>
<td>Acetic acid</td>
<td>8.7</td>
<td>8.7</td>
</tr>
</tbody>
</table>

### Derivatives of 4-nitro-1-hydroxy-2-naphthoic acid

<table>
<thead>
<tr>
<th>M.P.</th>
<th>Appearance</th>
<th>Solvent</th>
<th>Nitrogen analysis (micro)</th>
<th>Required Nitrogen (micro)</th>
</tr>
</thead>
<tbody>
<tr>
<td>114-15°</td>
<td>Pale yellow needles</td>
<td>Rectified spirit</td>
<td>4.3 per cent.</td>
<td>4.5</td>
</tr>
<tr>
<td>101-2°</td>
<td>Long pale yellow needles</td>
<td>Rectified spirit</td>
<td>5.1</td>
<td>5.1</td>
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<tr>
<td>170-1° (decom.)</td>
<td>Pale yellow needles</td>
<td>Benzene</td>
<td>8.7</td>
<td>8.7</td>
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<tr>
<td>138-10°</td>
<td>Thick pale yellow needles</td>
<td>Acetic acid</td>
<td>8.3</td>
<td>8.3</td>
</tr>
<tr>
<td>164-5°</td>
<td>Pale yellow needles</td>
<td>Acetic acid</td>
<td>8.3</td>
<td>8.3</td>
</tr>
</tbody>
</table>

- **1. Phenyl ester**
- **2. Ethyl ester**
- **3. Anilide**
- **4. p-Toluidide**
- **5. m-Toluidide**
- **6. o-Toluidide**
- **7. Phenyl ester**
- **8. Ethyl ester**
- **9. Anilide**
- **10. o-Toluidide**
- **11. m-Toluidide**
- **12. p-Toluidide**
in yellow needles, was filtered and dried over phosphorus pentoxide under reduced pressure, m.p. 103-4°.

[Found : Cl, 13.3 ; C_{12}H_8O_4 NCl requires Cl, 13.4 per cent.]

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