Ceric Ammonium Nitrate Oxidation of Polynuclear Aromatic Hydrocarbons to Quinones

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The amazing oxidizing power of ceric ammonium nitrate \([\text{(NH}_4\text{)}_2\text{Ce(NO}_3\text{)}_6; \text{CAN}]\) has been demonstrated by a series of oxidation reactions of organic compounds. For example, cyclic ketones undergo ring fission to produce nitratocarboxylic acids (except adamantane which affords a lactone)\(^1\), benzoins are split into an aldehyde and a carboxylic acid\(^2\), dithioacetals are degraded to carbonyl compounds\(^3\), diaryl sulfides are oxidized to sulfoxides\(^4\), carboxylic acid hydrazides are cleaved to the parent acids\(^5\), and dihydric phenols are oxidized to quinones\(^6\).

Quinones have been obtained in moderate yields from chromic acid oxidation of polycyclic aromatic hydrocarbons, e.g., 1,4-naphthoquinone (18-22\% yield)\(^7\) and phenanthrene-9,10-quinone (44-48\% yield)\(^8\). The reaction requires either prolonged periods of standing or elevated temperatures for its completion. Now we have found that oxidation with ceric ammonium nitrate proceeds quite readily, giving moderate yields.

### Table. CAN Oxidation of Aromatic Hydrocarbons

<table>
<thead>
<tr>
<th>Arene</th>
<th>Reaction Conditions</th>
<th>Quinone</th>
<th>Yield (%)</th>
<th>m.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Chemical Structure]</td>
<td>25°, 5 min</td>
<td>![Chemical Structure]</td>
<td>20</td>
<td>123-125°</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td>25°, 5 min</td>
<td>![Chemical Structure]</td>
<td>61</td>
<td>284-286°</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td>60°, 30 min</td>
<td>![Chemical Structure]</td>
<td>27.4</td>
<td>205-207°</td>
</tr>
<tr>
<td>![Chemical Structure]</td>
<td></td>
<td>![Chemical Structure]</td>
<td>11.5</td>
<td>152-155°</td>
</tr>
</tbody>
</table>

### Oxidation of Aromatic Hydrocarbons; General Procedure:

The hydrocarbon (1 mmol) was dissolved in 75\% aqueous tetrahydrofuran (8 ml) and treated with CAN (2.2 g. 4 mmol) under the conditions given in the Table. After the reaction was completed, the mixture was diluted with water, and exhaustively extracted with benzene. Products were obtained from the organic extracts by evaporation. Anthraquinone was purified by recrystallization from glacial acetic acid. Naphthoquinone and the phenanthrenequinones were isolated by thick-layer chromatography on silica gel, and identified by comparison with authentic samples.

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