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OXIDATION OF ARYLPROPENES BY
2,3-DICHLORO-5,6-DICYANOBENZOQUINONE (DDQ)

A DISSERTATION SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN CHEMISTRY
DECEMBER 1970

by
Frank Edward Lutz

DISSERTATION COMMITTEE:
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PLEASE NOTE:

Some pages have small
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And whatsoever ye do, do it heartily as to the Lord, and not unto men...

Colossians 3:23

For now we see through a glass, darkly; but then face to face: now I know in part, but then shall I know even as also I am known.

1 Corinthians 13:12
ACKNOWLEDGMENTS

I would like to thank Mr. Alfred E. Asato for fruitful, thought-provoking discussions of several areas concerning this work, and Mr. K. N. Somasekharan for clarification of various theoretical ideas through his clear and concise thinking on matters of this kind. I also express my appreciation to Mr. Thomas J. Levek who, together with Messrs. Asato and Somasekharan and others in the laboratory, provided much mirth and merriment from time to time, creating a pleasant atmosphere in which to work.

Grateful acknowledgment is also made to the Petroleum Research Fund, administered by the American Chemical Society, in support of this research for two years.
ABSTRACT

The oxidation of arylpropenes by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has been studied, the objective being determination of the mechanism and scope of the reaction. Instantaneous molecular complex formation, attributed to the high electron affinity of DDQ, preceded chemical reaction in all cases. The arylpropenes anethole and estragole, were oxidized to 2,3-dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (I) and 2,3-dichloro-5,6-dicyanohydroquinone mono(1-p-anisylpropenyl) ether (X), respectively. S-Methylstyrene was oxidized to 2,3-dichloro-5,6-dicyanohydroquinone mono- and di-cinnamyl ethers (XI and XIII). α-Methylstyrene gave no reaction.

\[
\begin{align*}
\text{Anethole} & \quad \text{Estragole} \quad \beta - \text{Methylstyrene} \\
\text{I} & \quad \text{X} \quad \text{XII} \quad \text{XIII}
\end{align*}
\]
Based on relative rate data, electron paramagnetic resonance results, and the nature of the reaction products, a hydride-ion abstraction reaction mechanism is proposed.

In an analogous fashion the hydroquinone ethers underwent further oxidation by DDQ, leading to acetics, which rapidly hydrolyzed to \( \text{p-methoxycinnamaldehyde} \) or cinnamaldehyde. Ethers I and X also underwent cleavage with hydrochloric acid and solvolysis with alcohol yielding \( \text{p-methoxycinnamyl chloride} \) and unknown \( 1-(\text{p-anisyl})-1\)-alkoxypropenes respectively. It is proposed that the latter form via a cyclic Sn2' mechanism. Finally, the arylpropenes are suggested to be slightly susceptible to charge-transfer polymerization by DDQ.
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<th>Description</th>
<th>Page</th>
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</thead>
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<td>157</td>
</tr>
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</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Although 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has been known for more than half a century, it has only been within the past few years that its exceptional oxidizing ability has been recognized (Table I). In 1954 Braude, Linstead, and Jackman investigated the efficacy of the quinone in dehydrogenating hydroaromatic compounds. It proved excellent for the purpose and was highly recommended. Eight years later Ringold and Turner used DDQ for introduction of double bonds into steroidal ketones, a process known to enhance the biological activity of such compounds. This proved to be the beginning of the most extensive use of this quinone, giving rise to literally hundreds of examples in the literature to date. Most recently it has been employed by Becker in the one-electron oxidation of phenols.

A. OXIDATION BY DDQ--LITERATURE SURVEY

Scope. The introduction of a double bond by hydride abstraction followed by proton elimination from a suitable substrate (dehydrogenation) constitutes the primary reaction of DDQ. With appropriately ortho-substituted benzenes cyclization often accompanies the dehydrogenation. A secondary reaction of growing significance involves substrates containing allylic and/or benzylic hydrogens wherein dehydrogenation is blocked. In these cases cations and
<table>
<thead>
<tr>
<th>REACTION</th>
<th>DESCRIPTION</th>
<th>SOURCE</th>
</tr>
</thead>
</table>
| \[
\text{HCl} + \text{HCN} \rightarrow \text{DDQ}
\] | PREPARATION | THIELE and GUNTHER 1906 |
| \[
\text{C}_{6}\text{H}_{5} \rightarrow \text{DDQ} \rightarrow \text{DDHQ}
\] | DEHYDROGENATION OF HYDROAROMATIC COMPOUNDS | BRAUDE, LINSTEAD and JACKMAN -- 1954 |
| \[
\text{Aprotic}
\] | DEHYDROGENATION OF STEROIDS | RINGOLD and TURNER 1962 |
| \[
\text{Protic}
\] | PHENOL OXIDATION | BECKER -- 1965 |
| \[
\text{arylpropene} \rightarrow \text{DDQ}
\] | ARYLPROPENE OXIDATION | KIEFER and LUTZ 1970 |
radicals are formed which have been isolated in a few cases but generally lead to coupled products (substrate-substrate or substrate-quinone). Table II summarizes a few representative examples of these reaction types.

**Mechanism.** The mechanism of dehydrogenation has been well explained. In a series of papers on hydroaromatic compounds, Braude, Linstead, and Jackman proved that a two-step, ionic process with rate-determining hydride ion transfer to the quinone, followed by rapid proton loss from the substrate was involved.\(^6,7,8\) This is illustrated in Scheme I for the dehydrogenation of acenaphthene by DDQ. Trost, on reinvestigation of this mechanism, concluded that tight ion-pairs must also be incorporated to explain observed stereochemical results (net cis dehydrogenation).\(^9\) Turner and Ringold have shown that 3-keto- and \(\Delta^4\)-3-keto steroids dehydrogenate through the

**SCHEME I**
### TABLE II
**REPRESENTATIVE EXAMPLES OF DDQ OXIDATION**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dehydrogenation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steroidal ketones</td>
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</tr>
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<td><img src="image1" alt="Chemical Structures" /></td>
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<td>10</td>
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</tr>
<tr>
<td><img src="image3" alt="Chemical Structures" /></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structures" /></td>
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</tr>
<tr>
<td><img src="image5" alt="Chemical Structures" /></td>
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TABLE II - Continued

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<tr>
<th>Substrate</th>
<th>Dehydrogenation</th>
<th>Ref.</th>
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<tr>
<td><strong>Alcohols</strong></td>
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</tr>
<tr>
<td><img src="image1" alt="Alcohol Structure" /> → <img src="image2" alt="Alcohol Structure" /></td>
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<td></td>
</tr>
<tr>
<td><img src="image3" alt="Alcohol Structure" /> → <img src="image4" alt="Alcohol Structure" /></td>
<td>13</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Alcohol Structure" /> → <img src="image6" alt="Alcohol Structure" /></td>
<td>14</td>
<td></td>
</tr>
<tr>
<td><strong>Phenols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image7" alt="Phenol Structure" /> → <img src="image8" alt="Phenol Structure" /></td>
<td>15</td>
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</tr>
<tr>
<td><strong>Steroidal lactones</strong></td>
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</tr>
<tr>
<td><img src="image9" alt="Steroidal Lactone Structure" /> → <img src="image10" alt="Steroidal Lactone Structure" /></td>
<td>16</td>
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</table>
TABLE II - Continued

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Dehydrogenation</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td><strong>Nitrogen Heterocycles</strong></td>
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<tr>
<td><img src="image1" alt="N-Heterocycle" /> → <img src="image2" alt="Pyridine" /></td>
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<td>17</td>
</tr>
<tr>
<td><img src="image3" alt="N-Heterocycle" /> → <img src="image4" alt="Pyridine" /></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td><strong>Hydroaromatic compounds</strong></td>
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<tr>
<td><img src="image5" alt="Cyclohexene" /> → <img src="image6" alt="Cyclohexene" /></td>
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<td>19</td>
</tr>
<tr>
<td><img src="image7" alt="Cyclohexene" /> → <img src="image8" alt="Cyclohexene" /></td>
<td></td>
<td>20</td>
</tr>
<tr>
<td><img src="image9" alt="Cyclohexene" /> → <img src="image10" alt="Cyclohexene" /></td>
<td></td>
<td>19</td>
</tr>
<tr>
<td><strong>Alkenes</strong></td>
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<td><img src="image11" alt="Alkene" /> → <img src="image12" alt="Alkene" /></td>
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TABLE II - Continued

<table>
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<th>Dehydrogenation</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td><strong>Alkenes - continued</strong></td>
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<tr>
<td><img src="image" alt="Image of cymene dehydrogenation" /></td>
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<td>19</td>
</tr>
<tr>
<td><strong>Ortho-substituted benzenes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Image of ortho-substituted benzene dehydrogenation" /></td>
<td><img src="image" alt="Image of dehydrogenation product" /></td>
<td>22</td>
</tr>
<tr>
<td><img src="image" alt="Image of 2,3-substituted quinone dehydrogenation" /></td>
<td><img src="image" alt="Image of dehydrogenation product" /></td>
<td>23</td>
</tr>
<tr>
<td><strong>2,3-Substituted Quinones</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Image of 2,3-substituted quinone dehydrogenation" /></td>
<td><img src="image" alt="Image of dehydrogenation product" /></td>
<td>24</td>
</tr>
</tbody>
</table>
TABLE II - Continued

<table>
<thead>
<tr>
<th>Substrate</th>
<th>H(^-) of H(^+) Abstraction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td></td>
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</tr>
<tr>
<td><img src="image1" alt="Phenol structure" /></td>
<td><img src="image2" alt="Phenol reaction" /></td>
<td>25</td>
</tr>
<tr>
<td><img src="image3" alt="Phenol structure" /></td>
<td><img src="image4" alt="Phenol reaction" /></td>
<td>25</td>
</tr>
<tr>
<td>Veratrole</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Veratrole structure" /></td>
<td><img src="image6" alt="Veratrole reaction" /></td>
<td>26</td>
</tr>
<tr>
<td>Perinaphthene</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image7" alt="Perinaphthene structure" /></td>
<td><img src="image8" alt="Perinaphthene reaction" /></td>
<td>27</td>
</tr>
</tbody>
</table>
**TABLE II - Continued**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$H^-$ of $H\cdot$ Abstraction</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tropylidene</td>
<td><img src="image1" alt="Tropylidene Reaction" /></td>
<td>27</td>
</tr>
<tr>
<td>1,2,3-Triphenylcyclopropene</td>
<td><img src="image2" alt="1,2,3-Triphenylcyclopropene Reaction" /></td>
<td>27</td>
</tr>
<tr>
<td>Acridine</td>
<td><img src="image3" alt="Acridine Reaction" /></td>
<td>27</td>
</tr>
<tr>
<td>2,2-Dimethylindane</td>
<td><img src="image4" alt="2,2-Dimethylindane Reaction" /></td>
<td>28</td>
</tr>
</tbody>
</table>
enol with hydride abstraction occurring from the 1 position in the latter case but not necessarily so in the former case. In both cases enolization proceeded via the 2β proton (Equations 1 and 2).

$$\text{HO} \rightleftharpoons \begin{array}{c} \text{DDQ} \downarrow \text{HO} \end{array} \quad (1)$$

$$\text{HO} \rightleftharpoons \begin{array}{c} \text{DDQ} \downarrow \text{HO} \end{array} \quad (2)$$

 Allylic and benzylic alcohols dehydrogenate in a related manner yielding carbonyl compounds.  

$$\begin{align*}
\text{C}=\text{C}-\text{CH}-\text{OH} & \xrightarrow{\text{DDQ}} \text{C}=\text{C}-\text{C}=\text{O} \\
\text{C}=\text{C}-\text{CH}-\text{OH} & \xrightarrow{\text{DDH}} \text{C}=\text{C}-\text{C}=\text{O} \\
\text{C}=\text{C}-\text{CH}-\text{OH} & \xrightarrow{\text{DDQ}} \text{C}=\text{C}-\text{C}=\text{O} \\
\text{C}=\text{C}-\text{CH}-\text{OH} & \xrightarrow{\text{DDQ}} \text{C}=\text{C}-\text{C}=\text{O} \\
\end{align*}$$  

(3)

The mechanism for oxidation of those substrates in which dehydrogenation is blocked is of current controversy. In their work on blocked hydroaromatic compounds, Braude, et al. observed a coupling reaction between DDQ and 2,2-dimethylindane. Based on mechanistic details obtained for other hydroaromatic systems (notably 1,1-dimethylhydrodronaphthalene) they concluded that an ionic process was involved (Scheme I). On the other hand, Becker observed a similar reaction with diphenylmethane (Equation 4) and put forth a free radical mechanism to explain the result. However, the inference of a one-electron process was based solely on analogy with his work on phenol oxidation via DDQ. The two systems are not
comparable, as hydride abstraction is most improbable in the latter case. Thus one group contends this type of oxidation to be a radical process while another believes it ionic in nature. The present work clarifies this matter considerably.

Since DDQ is a highly electron-deficient molecule, it readily enters into complex formation (Table III), as indicated by intense color changes which occur in solution on mixing with an electron-rich molecule (e.g. benzene). Thus most oxidative reactions affected by this quinone are accompanied by complex formation.
## TABLE III

**MOLECULAR COMPLEXES OF DDQ WITH ORGANIC DONOR MOLECULES**

<table>
<thead>
<tr>
<th>Donor (solvent)$^a$</th>
<th>$\lambda_{ct}$ (nm)$^b$</th>
<th>$K_C$</th>
<th>Resistivity$^d$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene$^x$</td>
<td>410</td>
<td></td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Benzene (CHC$_3$I$_3$)</td>
<td>27 (2486)$^e$</td>
<td>0.47</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>440 (1366)</td>
<td>0.96</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Naphthalene(CHC$_3$I$_3$)</td>
<td>470 (1364)</td>
<td>3.26</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>625</td>
<td>2.40</td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>584 (720)</td>
<td>21.9</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Phenanthrene(CHC$_3$I$_3$)</td>
<td>582 (2000)</td>
<td>14.54</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>m-Terphenyl (CHC$_3$I$_3$)</td>
<td>574 (900)</td>
<td>2.70</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>622 (3537)</td>
<td>14.5</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Fluorene (CHC$_3$I$_3$)</td>
<td>630 (1666)</td>
<td>14.60</td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>Chrysene</td>
<td>650 (1337)</td>
<td>14.8</td>
<td></td>
<td>34</td>
</tr>
<tr>
<td>Chrysene (CHC$_3$I$_3$)</td>
<td>600 (1250)</td>
<td>23.45</td>
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<td>32</td>
</tr>
<tr>
<td>Pyrene (CHC$_3$I$_3$)</td>
<td>540 (1249)</td>
<td>19.01</td>
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<td>32</td>
</tr>
<tr>
<td>Pyrene</td>
<td>550 (2176)</td>
<td>9.4 $^f$</td>
<td>$1 \times 10^6$</td>
<td>34</td>
</tr>
<tr>
<td>Perylene</td>
<td></td>
<td>$3 \times 10^6$</td>
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<td>35</td>
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<tr>
<td>Thianthrene</td>
<td>690</td>
<td></td>
<td></td>
<td>36</td>
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<tr>
<td>Dibenzo(c,d)phenothiazine</td>
<td></td>
<td>$5 \times 10^6$</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>Dibenzo(c,d)phenothiazine (2:1)</td>
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<td>17.0</td>
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<tr>
<td>10-Methylphenothiazine (CH$_3$I$_3$)</td>
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<td></td>
<td>36</td>
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<tr>
<td>Toluene (CHC$_3$I$_3$)</td>
<td>450 (2332)</td>
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<tr>
<td>Toluene</td>
<td>459</td>
<td></td>
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<td>38</td>
</tr>
<tr>
<td>Donor (solvent)(^a)</td>
<td>(\lambda_{ct}) (nm)(^b)</td>
<td>(K_c)(^c)</td>
<td>Resistivity(^d)</td>
<td>Ref</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------</td>
<td>-------------</td>
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</tr>
<tr>
<td>o-Xylene</td>
<td>485</td>
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</tr>
<tr>
<td>m-Xylene</td>
<td>485</td>
<td></td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>526</td>
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<td>38</td>
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<tr>
<td>Mesitylene</td>
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<td>38</td>
</tr>
<tr>
<td>Durene</td>
<td>595</td>
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<td></td>
<td>38</td>
</tr>
<tr>
<td>Durene</td>
<td>589 (2000)</td>
<td>10.7(^f),(^i)</td>
<td></td>
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<tr>
<td>Durene</td>
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<td>9.1(^h),(^i)</td>
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<td>39</td>
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<tr>
<td>Pentamethylbenzene</td>
<td>596</td>
<td></td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>Pentamethylbenzene</td>
<td>595 (2860)</td>
<td>17.3(^f),(^i)</td>
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<tr>
<td>Pentamethylbenzene</td>
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<td>17.6(^h),(^i)</td>
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</tr>
<tr>
<td>Hexamethylbenzene</td>
<td>629 (3,260)</td>
<td>97.5</td>
<td></td>
<td>39</td>
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<tr>
<td>Hexamethylbenzene</td>
<td>621 (3660)</td>
<td>33.9(^f),(^i)</td>
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<tr>
<td>Hexamethylbenzene</td>
<td></td>
<td>33.9(^h),(^i)</td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>Hexamethylbenzene ((C_6H_{12}))</td>
<td>620</td>
<td></td>
<td></td>
<td>40</td>
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<tr>
<td>Tetrahydrofuran(^*)</td>
<td>355 (1800)</td>
<td>0.53</td>
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<td>41</td>
</tr>
<tr>
<td>Tetrahydropyran(^*)</td>
<td>365 (1750)</td>
<td>0.42</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>p-Dioxane(^*)</td>
<td>380 (1950)</td>
<td>0.40</td>
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<td>41</td>
</tr>
<tr>
<td>p-Dioxane(^*)</td>
<td>390</td>
<td></td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>Anisole</td>
<td>559</td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>1,2-Dimethoxybenzene</td>
<td>645</td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>1,3-Dimethoxybenzene</td>
<td>625</td>
<td></td>
<td></td>
<td>42</td>
</tr>
<tr>
<td>1,4-Dimethoxybenzene</td>
<td>714</td>
<td></td>
<td></td>
<td>42</td>
</tr>
</tbody>
</table>
TABLE III - Continued

<table>
<thead>
<tr>
<th>Donor (solvent)a</th>
<th>$\lambda_{ct}$(nm)$^b$</th>
<th>$K_c$$^c$</th>
<th>Resistivity$^d$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,3-Trimethoxy-benzene</td>
<td>565</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1,2,4-Trimethoxy-benzene</td>
<td>776</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trimethoxy-benzene</td>
<td>614</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1,2,3,5-Tetra-methoxybenzene</td>
<td>676</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>1,2,4,5-Tetra-methoxybenzene</td>
<td>942</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>Pentamethoxy-benzene</td>
<td>704</td>
<td></td>
<td>42</td>
<td></td>
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<tr>
<td>Hexamethoxy-benzene</td>
<td>578</td>
<td></td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>p-Phenylenediamine</td>
<td>$1 \times 10^6$</td>
<td></td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>1,6-Diaminopyrene</td>
<td>500</td>
<td></td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>2,5-Diethoxy-p-benzoquinone</td>
<td>440</td>
<td></td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>2,5-bis-N-methyl-amino-p-benzoquinone</td>
<td>683</td>
<td></td>
<td>44</td>
<td></td>
</tr>
</tbody>
</table>

a 1:1 complex unless otherwise specified; Solvent is CH$_2$Cl$_2$ unless noted otherwise; *indicates donor molecule also solvent.
b Parenthetical values are molar absorptivities.
c Association constant at 25° unless otherwise noted; averaged values determined by Benesi-Hildebrand method with $[D] > [A]$ or $[A] > [D]$ unless otherwise indicated (see H. A. Benesi and J. H. Hildebrand, J. Amer. Chem. Soc., 71, 2703 (1949)).
d At 25°, units are ohme-cm.
e Immediately after mixing, absorption time dependent.
f $[D] = [A]$.
g Ref. 35.
h Kinetic method, Ref. 39, $[D] >> [A]$.
i At 490.
Unfortunately, little work has been carried out on their role in reaction mechanisms as most efforts are still concentrated on characterizing the complexes.

Comparison with other reagents. Several studies of quinone reactivity have been made\(^2,4,45,46\) from which it has been observed that the reduction potential is a good measure of the electron affinity and, therefore, of the chemical reactivity of a quinone. Tetracyano-p-benzoquinone (TCNQ, cyananil) is thus predicted to be the most reactive quinone possible (Table IV) with the exception of the unknown tetracyano-o-benzoquinone.\(^4\) However, TCNQ and the two phenylsulfonylquinones listed are not readily available; DDQ thus becomes the highest potential quinone available for study. A quinone of high potential has the advantage of increased reaction rates which minimizes not only the reaction time but also the number of side reactions (e.g., 1,2- and 1,4- addition, concerted cycloaddition, substitution). Consequently, DDQ generally gives cleaner, higher-yield reactions than do other quinones.

Although many of the reactions of DDQ and selenium dioxide are similar, side reactions are much reduced with DDQ. In many cases selenium dioxide shows a propensity to enter into the substrate being dehydrogenated, necessitating deselenization procedures. The physiological action of the oxide is also known to resemble that of arsenic compounds, thus creating handling difficulties.\(^47\)

Manganese oxide has a high reduction potential of about 1.25 V,\(^48\) but in practice proves to be a mild oxidizing reagent and, therefore, does not have the versatility of DDQ. In addition the
### POLAROGRAPHIC REDUCTIONS OF QUINONES IN ANHYDROUS ACETONITRILE WITH 0.1M LITHIUM PERCHLORATE SUPPORTING ELECTROLYTE

<table>
<thead>
<tr>
<th>QUINONE b</th>
<th>$E_1$ (VOLTS) c</th>
<th>QUINONE b</th>
<th>$E_1$ (VOLTS) c</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="Image" alt="Structure" /> (+0.77) d</td>
<td><img src="Image" alt="Structure" /> +0.23</td>
<td><img src="Image" alt="Structure" /> +0.62 e</td>
<td><img src="Image" alt="Structure" /> +0.20 f</td>
</tr>
<tr>
<td><img src="Image" alt="Structure" /> +0.52</td>
<td><img src="Image" alt="Structure" /> +0.15</td>
<td><img src="Image" alt="Structure" /> +0.50</td>
<td><img src="Image" alt="Structure" /> -0.01</td>
</tr>
<tr>
<td><img src="Image" alt="Structure" /> +0.41</td>
<td><img src="Image" alt="Structure" /> -0.15</td>
<td><img src="Image" alt="Structure" /> +0.31</td>
<td><img src="Image" alt="Structure" /></td>
</tr>
</tbody>
</table>

(a) Taken from R.M. Schribner, J. Org. Chem., 31, 3671 (1966); (b) Quinones 1-5 x 10^{-4} M; (c) Vs Standard Calomel Electrode; (d) Estimate; (e) Graphite electrode; (f) Poorly defined wave.
oxide is used heterogeneously, requires activation in many cases, and must be used in large amounts for effective reaction.

Microorganisms are most selective in their reaction with organic substrates and have been used effectively for the introduction of \( \Delta^1 \) double bonds into \( \Delta^4 \)-3-ketones or \( \Delta^{4,6} \)-3-ketones.\(^ {49,50,51,52} \)
Yet even here DDQ is superior, for microbiological dehydrogenation requires large dilutions and special equipment that leads to handling difficulties.

B. PROBLEM BACKGROUND

In 1965 Wenski observed a new type of reaction: the dehydrogenation of arylpropenes by high-potential quinones.\(^ {53} \) Such a reaction was without precedent in the literature and was, therefore, investigated further. Anethole (1-\( \beta \)-anisylpropene) and isomeric estragole (3-\( \beta \)-anisylpropene) were the propenes of primary interest. Both occur naturally as summarized in Table V. DDQ was reported to react with anethole on a 1:2 mole bases forming DDHQ (96%) and a yellow solution of an unstable intermediate. Solvent removal resulted in polymerization. Chemical analysis of the yellow solution led to the conclusion that the intermediate (I) was a dehydrodimer of anethole having the carbon skeleton of isoanethole. (See Scheme III)
## TABLE V
NATURAL OCCURRENCE OF ANETHOLE AND ESTRAGOLE

<table>
<thead>
<tr>
<th>Source</th>
<th>% of Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil of Anise</td>
<td>85</td>
</tr>
<tr>
<td>Oil of Star Anise</td>
<td>90</td>
</tr>
<tr>
<td>Oil of <em>Clausena anisata</em></td>
<td>94</td>
</tr>
<tr>
<td>Oil of Bitter Fennel Seed</td>
<td>60</td>
</tr>
<tr>
<td>Oil of <em>Ocimum menthaefolium</em> Hochst.</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Other oils of family Umbelliferae</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Source</th>
<th>% of Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil of Basil</td>
<td>&gt;50</td>
</tr>
<tr>
<td>Oil of Estragon</td>
<td>65</td>
</tr>
<tr>
<td>Oil of Sweet Goldenrod</td>
<td>75</td>
</tr>
<tr>
<td>Oil of Bay</td>
<td>15</td>
</tr>
<tr>
<td>Oil of Anise</td>
<td>8</td>
</tr>
<tr>
<td>Oil of Star Anise</td>
<td>--</td>
</tr>
<tr>
<td>Oil of Bitter Fennel Seed</td>
<td>--</td>
</tr>
<tr>
<td>Oil of <em>Ocimum menthaefolium</em> Hochst.</td>
<td>--</td>
</tr>
<tr>
<td>Oil of <em>Ocimum canum</em> Sims</td>
<td>2</td>
</tr>
<tr>
<td>Oil of <em>Ocimum canum</em> Hybrid</td>
<td>18</td>
</tr>
</tbody>
</table>

---

SCHEME III

Anethole + DDQ (96%)

\[ \text{DDHQ} \]

\[ \text{H}_2, \text{Pd/C} \rightarrow \text{2 atm, 5 hr} \]

Isoanethole + Dihydroisoanethole (70%)

\[ \text{HBr, HOAc} \]

mp 126-127°

(lit. 126-127°)
These results suggested oxidative dimerization of olefins by high-potential quinones, a synthetic route of some interest to organic chemists. Consequently, it was decided to investigate this reaction further.

C. RESEARCH OBJECTIVES

On the basis of the foregoing discourse the research objectives were to

1) characterize the DDQ/anethole reaction by stabilization and structure elucidation of the reaction intermediate,
2) determine the mechanism for this reaction, and
3) investigate the scope of the reaction by use of arylpropenes and high-potential quinones other than those mentioned above.
CHAPTER II

EXPERIMENTAL SECTION

A. GENERAL INFORMATION

Recorded boiling points were determined at atmospheric pressure by the inverted capillary method\textsuperscript{55} and are corrected. Melting points were determined with a Fisher-Johns melting point block (uncorrected, rheostat setting 50) or with a modified Hershberg apparatus\textsuperscript{56} (corrected).

Ultraviolet absorption spectra were recorded with a Cary-14 double-beam recording spectrophotometer using 1 cm Silica cells.

Infrared spectra were run in potassium bromide or as liquid films on a Beckman Model IR-5A spectrophotometer. Bands are designated as strong(S), medium(M), weak(W), broad(B), and shoulder(sh).

Nuclear magnetic resonance spectra were obtained on Varian Associates A-60 or HA-100 spectrometers, using tetramethylsilane (TMS) as internal reference and field-frequency lock respectively. Chemical shifts are recorded in parts per million as \( \delta \) values. Signal multiplicities are designated as singlet(s), doublet(d), triplet(t), quartet(q), quintet(qn), sextet(sx), septet(sp), and multiplet(m).

Mass spectra were recorded by Sr. Mary Roger (Brennan) on a Hitachi Perkin-Elmer RMU-6D single focusing mass spectrometer using a direct inlet system.
Analytical gas chromatographic separation (glpc) were performed on a Varian Aerograph Model 200 gas chromatograph at 185° using a ¼ in. x 5 ft column packed with 20% SE-30 on 60-80 mesh Chrom W.

Column chromatograph employed columns slurry-packed with silica gel (Baker) or Florisil (100/200 mesh) as noted. Column dimensions indicated refer to the size of the adsorbent column within the supporting glass column.

Elemental analyses were performed at the Berkeley Analytical Laboratory, California, or (less often) by C. F. Geiger, 312 East Yale St., Ontario, California, as noted.

Commercially available Reagent or Analytical Reagent Grade solvents were used throughout without further purification.

All reactions were conducted at room temperature unless otherwise specified.

B. PURIFICATION AND CHARACTERIZATION OF REACTANTS

2,3-Dichloro-5,6-Dicyanobenzoquinone (DDQ). DDQ was conveniently recrystallized in 60 g quantities from benzene/petroleum ether (30°-60°), based on the approximate solubility figure of 10 g DDQ/100 ml benzene and a benzene/petroleum ether ratio of 3:2. Thus 600 ml of benzene was rapidly added to 65 g of commercial DDQ (Arapahoe Chemical Co.) with swirling. Stirring continued until all red particles had gone into solution. The resultant turbid solution was filtered (Büchner) to remove about 1 g of insoluble impurities (mostly DDHQ). The clear red filtrate was heated to boiling, 420 ml of petroleum ether added, and the mixture cooled at 4° for 1 hr after
which the crystals were separated, washed with petroleum ether, and dried under an infrared lamp. (The material crystallizes as a molecular-complex with benzene; the blood-red needles revert to bright yellow DDQ as the benzene evaporates.) Yield: 45 g. Excess solvents were removed from the filtrate in vacuo, the solution reheated, petroleum ether added to the turbidity point, and the mixture then cooled to recover an additional 15 g as a second crop. Total recovery was 60 g (93%), mp 213-215°. Recrystallization from methylene chloride has also been reported and gives rise to material of a different crystalline structure. DDQ may also be purified by sublimation at 150° and 0.08 mm Hg. The shelf-life of the quinone was approximately 4 months with gradual reduction to DDHQ occurring thereafter. Decomposition is accelerated by light; DDQ should therefore be stored in the dark. Spectroscopic material used below was recrystallized three times to a constant melting point of 215-216° (lit. 214-215°).

Ultraviolet spectrum (Figure 1):

Molecular complex maxima were as follows: Benzene, 407 (2,060), lit. 31 410; dry p-Dioxane, lit. 41 380; Acetonitrile, 345 (1,180); and Methanol, 345 nm (500). Additional maxima in acetonitrile were 226 (13,600), 271 (10,000), and 280 nm (10,000); in methanol 263 (6,140) and 290 nm (7,720); and in p-dioxane 267 nm (6,360).

Infrared spectrum (KBr, Figure 2):

723 (M, C-C-C in-plane bend), 803 (S, C-C-C out-of-plane bend), 895 (M), 1175 (S), 1265 (M, C-C stretch), 1550 (S,
Figure 1. UV Spectrum of 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) in Benzene (---) at $1.270 \times 10^{-4}$M, p-Dioxane (- - ) at $1.320 \times 10^{-4}$M, Acetonitrile (....) at $6.600 \times 10^{-5}$M, and Methanol (-----) at $6.602 \times 10^{-5}$M.
Figure 2. Top: IR Spectrum of 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ).
Bottom: IR Spectrum of Tetrachloro-2-benzoquinone (TCQ).
Figure 3. Top: 70eV Mass Spectrum of 2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ).
Bottom: 70eV Mass Spectrum of Tetrachloro-p-benzoquinone (TCQ).
Figure 4. UV Spectrum of Tetrachloro-$p$-benzoquinone (TCQ) in Benzene (---) at $1.465 \times 10^{-4}$M, and in $p$-Dioxane (---) at $6.100 \times 10^{-5}$M.
C=C stretch), 1670 (S, C=O stretch), and 2225 cm\(^{-1}\) (W, C≡N stretch). Assignments are after Baruah, Singh, and Jayaswal\(^{57}\) and agree with those reported elsewhere.\(^4\)

Mass spectrum (70eV, Figure 3):

m/e 226 (M\(^{+}\)), 87 (base). Reduction to DDHQ occurred during a normal scan.

Hückel calculations for DDQ were carried out using the HK-5 program\(^{58}\) which gave the results tabulated in Table VI.

**Tetrachloro-p-benzoquinone (chloranil).** Chloranil was re-crystallized from benzene/petroleum ether (30\(^{0}\)-60\(^{0}\)) by dissolving 25 g of crude commercial material in 600 ml of hot benzene, filtering off insoluble material, adding 150 ml of petroleum ether, and cooling at 4\(^{0}\) for 1 hr. Yield: 17 g, short, shiny, yellow needles. Removal of excess solvents from the filtrate in vacuo and repetition of the procedure gave an additional 3 g as a second crop. Recovery 20 g (80\%), mp 290\(^{0}\) (lit.\(^{59}\) 290\(^{0}\)).

**Ultraviolet spectrum (Figure 4):**

- In benzene -- \(\lambda_{\text{max}}\) 335 nm (1,226)
- In p-dioxane -- \(\lambda_{\text{max}}\) 330 sh (2,320) and 286 nm (14,030).

**Infrared spectrum (KBr, Figure 2):**

711 (S), 752 (S, C-C-C in-plane bend), 905 (M), 1106 (S, C-Cl stretch), 1206 (W), 1231 (W), 1255 (M, C-C stretch), 1560 (M, C=C stretch) and 1672 cm\(^{-1}\) (S, C=O stretch).

Assignments are after Baruah, Singh, and Jayaswal\(^{57}\).
### TABLE VI

**Hückel Molecular Orbital Parameters for DDQ**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coulomb&lt;sup&gt;a&lt;/sup&gt; Integral</th>
<th>Resonance&lt;sup&gt;α&lt;/sup&gt; Integral</th>
<th>q&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>F&lt;sub&gt;i&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>P&lt;sub&gt;ij&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;(bond)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α</td>
<td>β</td>
<td>0.260</td>
<td>0.198</td>
<td>0.376(1,2)</td>
</tr>
<tr>
<td>2</td>
<td>α</td>
<td>0.8β e</td>
<td>0.153</td>
<td>0.263</td>
<td>0.427(1,6)</td>
</tr>
<tr>
<td>3</td>
<td>α</td>
<td>0.8β e</td>
<td>0.153</td>
<td>0.263</td>
<td>0.695(2,3)</td>
</tr>
<tr>
<td>5</td>
<td>α</td>
<td>β</td>
<td>0.081</td>
<td>0.363</td>
<td>0.797(5,6)</td>
</tr>
<tr>
<td>6</td>
<td>α</td>
<td>β</td>
<td>0.081</td>
<td>0.363</td>
<td>0.731(1,7)</td>
</tr>
<tr>
<td>7</td>
<td>α+β</td>
<td>β</td>
<td>-0.391</td>
<td>1.000</td>
<td>0.398(2,8)</td>
</tr>
<tr>
<td>8</td>
<td>α+.6β</td>
<td>β</td>
<td>0.216</td>
<td>0.479</td>
<td>0.145(6,12)</td>
</tr>
<tr>
<td>12</td>
<td>α+2β</td>
<td>0.4β</td>
<td>-0.979</td>
<td>1.59</td>
<td>0.856(8,13)</td>
</tr>
<tr>
<td>13</td>
<td>α+1.2β e</td>
<td>β</td>
<td>-0.339</td>
<td>0.876</td>
<td></td>
</tr>
</tbody>
</table>

\[ E_{\text{Homo}} = E_8 = \alpha + 0.914\beta \]

\[ E_{\text{Lumo}} = E_9 = \alpha + 0.384\beta \]

Total \( E_\pi = 14\alpha + 28.903\beta \)

---


<sup>b</sup> Charge on atom i.

<sup>c</sup> Free valence index of atom i.

<sup>d</sup> Mobil \( \pi \)-bond order for bond ij.

Mass spectrum (70eV, Figure 3):
\[ m/e 244 \ (M^+) \], 87 (base).

l-p-Anisylpropene (anethole). Anethole was purified by distillation (235°) followed by drying over magnesium sulfate. The shelf life was about 4 days in a dark bottle. After this time colorless decomposition products formed and markedly reduced the reaction rate with DDQ.

Ultraviolet spectrum (p-Dioxane, Figure 5):
\[ \lambda_{\text{max}} \ 259 \ (20,150), \ 288 \ (2,470), \ 296 \ (2,330), \ \text{and} \ 307 \ \text{nm} (1,305). \ \text{Lit.}^{60} \ \lambda_{\text{max}} \ (95\% \text{ ethanol}) \ 258 \ (20,350) \ \text{and} \ 290 \ \text{nm} (2,280). \]

Infrared spectrum (Figure 6):
710 (W), 757 (M), 788 (S), 840 (S, \textit{para}-sub. aromatic), 944 (M), 966 (S, \textit{trans}-CH=CH-), 1038 (S), 1113 (M), 1175 (S), 1245 (S, C-O-C aromatic), 1283 (S), 1300 (M), 1347 (W), 1415 (W), 1444 (M), 1450 (M); 1460, 1508, 1570, and 1605 (M,S,W,S, aromatic), 2818 (M, aliphatic C-H), 2900 (M, aliphatic), and 2013 cm\(^{-1}\) (M, aromatic C-H). These values agree with those given in the literature.\(^{61}\)

Nuclear magnetic resonance spectrum (CCl\(_4\), 4\% w/v, Figure 7):
\[ \delta 6.70 \ (q, 4, J = 9.0 \text{ Hz}, -C_6H_4^-), \ 6.23 \ (d, 1, J_{\text{ab}} = 16.0 \text{ Hz}, H_a), \ 5.95 \ (d \text{ of } q, 1, H_b), \ 3.71 \ (s, 3, -OCH_3), \ \text{and} \ 1.83 \ (d, 3, J = 6.0 \text{ Hz}, -CH_3). \ \text{A reported spectrum lists coupling constants differing by +0.5 Hz from the above.}^{62} \]
Figure 5. Left: UV Spectrum of 1-β-Anisylpropene (Anethole) in β-Dikane.
Right: UV Spectrum of 3-β-Anisylpropene (Estragole) in Cyclohexane.
Figure 6. Top: IR Spectrum of 1-\(\pi\)-Anisylpropene (Anethole).
Bottom: IR Spectrum of 3-\(\pi\)-Anisylpropene (Estragole).
Figure 7. Top: NMR Spectrum of 1-p-Anisylpropene (Anethole) in CCl₄.
Bottom: NMR Spectrum of 3-p-Anisylpropene (Estragole) in CCl₄.
Figure 8. Top: 70 eV Mass Spectrum of 1-\(\alpha\)-Anisylpropene (Anethole).
Bottom: 70 eV Mass Spectrum of 3-\(\alpha\)-Anisylpropene (Estragole).
Mass spectrum (70eV, Figure 8):

\[ m/e \text{ } 148 \text{ (M}^+\text{, base).} \]

**3-p-Anisylpropene (estragole).** Commercially available estragole (Aldrich, \( n^20 \text{D } 1.5198 \)) was used without further purification. Spectroscopic data and glpc analysis of year-old material showed the absence of any \( p \)-methoxycinnamaldehyde, a compound reported present in aged estragole.\(^{63}\)

Ultraviolet spectrum (Cyclohexane, Figure 5):

\[ \lambda_{\text{max}} \text{ } 226 \text{ (7,480), 269 (1,100), 275 (1,360), 278 (1,500), 284 (1,400) and 292 nm (100).} \]

Infrared spectrum (Figure 6):

708 (W), 762 (W), 813 (M), 830 (M), 844 (M), 916 and 996 (M, M, -CH=CH\textsubscript{2}), 1040 (S), 1113 (W), 1178 (S), 1245 (S, aromatic C-O-C), 1300 (M), 1320 (W), 1438 (M); 1462, 1508, 1582 and 1610 (M, S, W, M, aromatic), 1646 (M, C=C), 2818 (W, aliphatic C-H), 2890 and 2982 (M, M, aliphatic), and 3050 cm\(^{-1}\) (M, aromatic C-H). Reported values agree with those found here.\(^{61}\)

Nuclear magnetic resonance spectrum (CCl\(_4\), 4\% w/v, Figure 7):

\[ \delta 6.83 \text{ (q, 4, J = 9.0 Hz, } -C_6H_4^-\text{), 5.86 (q of t, 1, } J_{ab} = 17.8 \text{ Hz, } J_{ac} = 9.6 \text{ Hz, } H_a), 4.96 (q of t, 1, } J_{bc} = 2.0 \text{ Hz, } J_{bd} = 1.6 \text{ Hz, } H_b), 4.96 (q of t, 1, } J_{cd} = 1.4 \text{ Hz, } H_c), 3.68 \text{ (s, 3, } -OCH_3\text{), and 3.25 (d, 2, } J_{ad} = 6.0 \text{ Hz, } H_d). \]
Mass spectrum (70eV, Figure 8):

m/e 148 (M⁺, base).

2-Phenylpropene (α-methylstyrene). Commercial α-methylstyrene was distilled at room temperature and 0.07 mm Hg and used without further purification.

Ultraviolet spectrum (Cyclohexane, Figure 9):

λmax 216 (5,800), 244 (7,180), 254 sh (5,450) and 262 nm (2870).

Lit. 64 λmax 215.4 (8,670) and 241.5 nm (9,780).

Infrared spectrum (Figure 10):

702 and 775 (S,S, monosub. aromatic), 890 (S, unsym. alkene), 1002 (W), 1028 (M), 1300 (W), 1370 (M), 1438 (M); 1490, 1565 and 1595 (M,W,W, aromatic), 1620 (M, C=C), 2940 (M, aliphatic), and 3030 cm⁻¹ (M, aromatic C-H).

Nuclear magnetic resonance spectrum (CCI₄, 5% w/v, Figure 11):

δ7.25 (m, 5, C₆H₅⁻), 5.26 (sx, 1, H_b), 4.98 (qn, 1, H_c) and 2.10 (d, 3, -CH₃). Reported coupling constants are:

J_cisoid = 1.5 Hz and J_transoid = 0.8 Hz. 65 (See reference 66 for highly resolved methyl signal.)

Mass spectrum (70eV, Figure 12):

m/e 118 (M⁺, base).
Figure 9. Left: UV Spectrum of 1-Phenylpropene (β-Methylstyrene) in p-Dioxane.
Right: UV Spectrum of 2-Phenylpropene (α-Methylstyrene) in Cyclohexane.
Figure 10. Top: IR Spectrum of 2-Phenylpropene (α-Methylstyrene).
Bottom: IR Spectrum of 1-Phenylpropene (β-Methylstyrene).
Figure 11. Top: NMR Spectrum of 2-Phenylpropene (α-Methylstyrene) in CCl₄.
Bottom: NMR Spectrum of 1-Phenylpropene (β-Methylstyrene) in CCl₄.
Figure 12. Top: 70 eV Mass Spectrum of 2-Phenylpropene (α -Methylstyrene).

Bottom: 70 eV Mass Spectrum of 1-Phenylpropene (β -Methylstyrene).
**1-Phenylpropene (β-methylstyrene).** Commercial β-methylstyrene (Aldrich, puriss. n\(^{20}_D\) = 1.5462) was used without further purification.

**Ultraviolet spectrum (p-Dioxane, Figure 9):**

\[ \lambda_{\text{max}} 251 (14,260), 274 (1,115), 283 (977) \text{ and } 293 \text{ nm (606)}. \]

Lit.\(^6\) \[ \lambda_{\text{max}} 250 (17,300) \text{ and } 293 \text{ nm (780)}. \]

**Infrared spectrum (Figure 10):**

- 692 and 734 (S,S, monosub, aromatic), 767 (W), 808 (W), 910 (W), 945 (M), 962 (S, trans-CH=CH-), 980 (M), 1030 (W), 1070 (M), 1094 (W), 1155 (W), 1178 (W), 1208 (W), 1276 (W), 1304 (W), 1330 (W), 1374 (W); 1440, 1493, 1575 and 1594 (S,M,W,W, aromatic), 1660 (W, C=C), 2830 and 2900 (W,M, aliphatic), and 3005 cm\(^{-1}\) (M, aromatic C-H).

**Nuclear magnetic resonance spectrum (CCl\(_4\), 5% w/v, Figure 11):**

- 6.715 (m, 5, C\(_6\)H\(_5\)-), 6.38 (d, 1, J\(_{ab}\) = 15.5 Hz, H\(_a\)),
- 6.04 (d of q, 1, J\(_{bx}\) = 5.5 Hz, H\(_b\), 1.85 (d, 3, J\(_{ax}\) = 1.5 Hz, -CH\(_3\)). Calculated coupling constants have been reported as follows: 67 J\(_{ab}\) = 15.6 Hz, J\(_{bx}\) = 6.6 Hz, and J\(_{ax}\) = 1.8 Hz.

**Mass spectrum (70eV, Figure 12):**

- m/e 118 (M\(^+\), base).

**p-Methoxystyrene.** Commercial material (Aldrich) was used without further purification.
C. OXIDATION OF ANETHOLE BY DDQ

1. Stoichiometry of the reaction.

Several reactions were run as described in Section C-2 on page 43 with the exception of a variable mole ratio of reactants. The results given in Table VII verify that the reaction proceeds on a 1:1 mole basis.

<table>
<thead>
<tr>
<th>Anethole (mmol)</th>
<th>DDQ (mmol)</th>
<th>Mole ratio</th>
<th>Amt. DDHQ&lt;sup&gt;a&lt;/sup&gt; (g)</th>
<th>Percent&lt;sup&gt;b&lt;/sup&gt; DDHQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>1:1</td>
<td>0.281</td>
<td>49.1</td>
</tr>
<tr>
<td>5.0</td>
<td>2.5</td>
<td>2:1</td>
<td>0.283</td>
<td>49.4</td>
</tr>
<tr>
<td>10.0</td>
<td>2.5</td>
<td>4:1</td>
<td>0.286</td>
<td>50.0</td>
</tr>
<tr>
<td>1.25</td>
<td>2.5</td>
<td>1:2</td>
<td>0.145</td>
<td>25.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> 2,3-Dichloro-5,6-dicyanohydroquinone.
<sup>b</sup> Based on DDQ.
2. Description -- 1:1 Mole Reaction.

Solution of 2,3-dichloro-5,6-dicyanohydroquinone bis-
(1-p-anisylpropenyl)ether(I). A solution of 3.72 ml (25 mmol) of freshly distilled anethole in 20 ml of benzene was added with swirling to a red solution of 5.67 g (25 mmol) of DDQ in 230 ml of benzene. On contact molecular complex formation produced a black solution which became yellow in 1 min with concomitant precipitation of 2.84 g (50%) of a mint-green solid. Vacuum filtration left a golden-yellow solution of 1.

Nuclear magnetic resonance spectrum of (I) in benzene-d₆.
The nuclear magnetic resonance solution spectrum of 1 (reaction repeated on a small scale in benzene-d₆, Figure 55) showed signals at 66.91 (q, 4, Jₐₚ = 9.0 Hz, -C₆H₄⁻), 6.42 (d, 1, Jₐₚ = 15.5 Hz, Hₐ), 6.18 (d of t, 1, Hₜ), 4.46 (d, 2, Jₕ = 6.0 Hz, -CH₂⁻) and 3.27 (s, 3, -OCH₃). This verified the presence of the p-methoxycinnamyl moiety in (I).

Identification of 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ). The mint-green solid isolated above was crystallized from 30% ethanol based on a solubility figure of 10 mg/ml. The crude material was dissolved in hot solvent, the yellow solution filtered away from trace insoluble polymeric material and then cooled at 4°C overnight. Very fine, light yellow needles formed which were recrystallized three more times, dried in an Abderhalden pistol at 100°C (P₂O₅; needles became light tan), and then sublimed (200°C, 0.06 mm Hg, 6 hr). Mp = 280°C (dec).
Ultraviolet spectrum (Figure 13):

In Methanol: $\lambda_{\text{max}}$ 247 (19,200), 267 sh (5,400) and 395 nm (8,020).

In p-Dioxane: $\lambda_{\text{max}}$ 257-265 (6,500) and 350 nm (7,500).

Infrared spectrum (KBr, Figure 14):

688 (W), 745 (M), 776 (M), 792 (W), 886 (S), 897 sh (S), 998 (W), 1075 (S), 1190 (S, C-O stretch), 1247 (S), 1275 (S), 1355 (M), 1448 (S, O-H bend), 1510 (W), 1570 (W), 2250 (S, C≡N stretch) and 3220 cm$^{-1}$ (S, O-H stretch).

Nuclear magnetic resonance spectrum (Figure 15):

The spectrum was difficult to determine as the hydroquinone exhibits a very weak, broad signal. Table VIII summarizes the conditions employed and results found. Figure 15 shows an illustrative example.

Mass spectrum (70eV, Figure 16):

$m/e$ 228 (M$,^+$, base).

TABLE VIII

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conc(w/v)</th>
<th>$\delta$-OH</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>15%</td>
<td>7.30</td>
<td>weak</td>
</tr>
<tr>
<td>DMSO</td>
<td>20%</td>
<td>10.70</td>
<td>broad</td>
</tr>
<tr>
<td>THF</td>
<td>20%</td>
<td>9.97</td>
<td>signal</td>
</tr>
</tbody>
</table>
Figure 13. UV Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ) in Methanol (---) at 2.495 x $10^{-5}$M, and in $p$-Dioxane (---) at approximately 3.93 x $10^{-5}$M.
Figure 14. IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ).
Figure 15. NMR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ) in THF.
Figure 16. 70 eV Mass Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ).
A final piece of structural information was obtained by preparation of the diacetate derivative of the hydroquinone. A 0.20 g portion of the solid was suspended in 5 ml of acetic anhydride and 2 drops of conc sulfuric acid added with vigorous stirring. On addition of the acid the solution turned intensely green as the solid went into solution. No further change was noted on stirring the mixture for 1 hr. At the end of this time the excess acetic anhydride was destroyed by dropwise addition of 5 ml of water with ice-bath cooling whereupon the crude acetate precipitated from solution as a tan solid (0.20 g, 74%). Recrystallization twice from 95% ethanol gave pale tan, short needles, mp 182-183° (lit.6 181-182°).

All of these data conclusively established that the mint-green solid was 2,3-dichloro-5,6-dicyanohydroquinone.

3. Attempted derivitization of 2,3-dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether(I).

**Hydroxylation.** Treatment of (I) with potassium permanganate (0.15 M) required the theoretical amount (67 ml) before any purple color would persist. However, after two minutes extensive gas evolution ensued; olfactory analysis indicated it was hydrogen cyanide. Removal of the solvent from the organic phase in vacuo gave only black polymer. Treatment of a known sample of DDHQ with the reagent also caused immediate generation of hydrogen cyanide.
Epoxidation. Treatment of (I) with 2.3 g of m-chloro-perbenzoic acid (81% active) in benzene by the method of Schwartz\textsuperscript{70} for 24 hrs at 30° followed by treatment with 10 ml of 10% perchloric acid for 3 hrs and removal of the solvent in vacuo from the resulting organic phase gave only intensely yellow polymer. m-Chlorobenzoic acid (1.0 g, mp 156-159°) was recovered from the acidified aqueous phase.

Hydrogenation. A 7.46 ml portion of anethole (50 mmol) was dissolved in 50 ml of benzene and added to 5.67 g of DDQ (25 mmol) in 150 ml of benzene. Fifty-one percent of the DDQ was precipitated as DDHQ within 1 min and removed by filtration to give an orange-yellow solution of (I). This was hydrogenated with the Parr apparatus and 0.26 g of 10% Palladium on carbon for 5 hrs at room temperature and 1 atm. Removal of the catalyst at the end of this time revealed that an additional 6% of DDQ had been returned as DDHQ during the hydrogenation. Evaporation of most of the solvent from the deep red filtrate revealed the presence of blue polymeric material. Distillation of this partial benzene solution of polymer at 0.5 mm Hg produced a pale yellow liquid at 55-65° and left a residue of hard intractable tar. Redistillation of the liquid at 0.08 mm Hg gave 1.10 g (15%) of colorless material boiling at 45-50°. Glpc indicated two components present in a
60:40 ratio. The nuclear magnetic resonance spectrum showed signals at 66.94 (q, 4, $J_{ab} = 9.0 \text{ Hz, } -\text{C}_6\text{H}_4-$), 6.32 (d, 1, $J_{ab} = 16.0 \text{ Hz, } H_a$), 5.98 (d of q, 1, $H_b$), 3.71 (s, 3, -OCH$_3$), 2.49 (t, 2, $J = 7.5 \text{ Hz, } -\text{CH}_2$), 1.82 (d, 3, $J = 5.5 \text{ Hz, } -\text{CH}_3$), 1.52 (m, 2, -CH$_2$), and 0.9 (t, 3, $J = 7.5 \text{ Hz, } -\text{CH}_3$) verifying the components as anethole and dihydroanethole respectively.

Repeating the above reaction on a 1:1 mole basis and hydrogenating the mixture at 2 atm for 18 hrs gave only polymer on solvent removal and attempted distillation.

Use of a semi-quantitative hydrogenation apparatus for hydrogenation of a 1:1 mole scale reaction showed that the initial rate of hydrogen uptake was 1 ml/min but fell to 1 ml/15 min in 1 hr and 1 ml/2 hrs in 24 hrs. In this case an 80:20 mixture of anethole and dihydroanethole was isolated in small amount from the polymer.

**Bromination.** The solution of (I) from a 10 mmol scale reaction was treated with a 1:5:6 mole ratio aqueous solution of potassium bromate, potassium bromide and sulfuric acid. The reaction mixture turned red, indicating excess bromine had been generated. Forty mmol of potassium iodide was added to the solution along with starch indicator and the solution back titrated with 1.00 N sodium thiosulfate. Calculations indicated an excess of 0.016 mmol of bromine, or that exactly 5 mmol of bromine had
reacted. Repeating the entire procedure with the exception of first running a blank again showed the absorption of only 5 mmol of bromine. Separation of phases in both cases, drying, and removal of solvent from the organic phase left only thick, greenish-brown polymer.

4. Identification of 2,3-dichloro-5,6-dicyanohydroquinone bis(1- p-anisylpropenyl) ether (I).

Isolation. As soon as the benzene solution of I was formed (Section D-2, p. 43), 50 ml of p-dioxane was added and the solution extracted 5 times with 50 ml of water. The extracts were cherry-red and contained trace amounts of DDHQ in suspension—they were discarded. The organic phase was dried (magnesium sulfate) and solvent removed in vacuo, leaving a yellowish solid. Addition of 50 ml of chilled methanol (10\(^\circ\)) produced a slurry as colored polymeric materials and trace amounts of DDHQ dissolved. Filtration through a coarse, cintered glass funnel followed by washing with cold methanol and bell-jar drying gave a 3.0-3.5 g (45-55\%) of very pale green, crude I. Evaporation of the methanol from the red filtrate and readdition of benzene separated an additional 0.15 g of DDHQ, leaving a dark red solution which on solvent removal and distillation (short path, 0.2 mm Hg, 47-54\(^\circ\)) gave 0.19 g of a mixture of methyl ethers (see Section D-3, p. 92). Approximately 5\% of I thus underwent methanolysis during isolation.
Crystallization. Crude I (Iso-I) was fractionally crystallized from p-dioxane/hexane based on a solubility figure of 50 mg/ml and a dioxane/hexane ratio of about 1:3. The material dissolved in dioxane with slight warming to give a yellow solution. This was heated until hot (not boiling), hexane added as per Table IX below (there is no lasting turbidity), and the solution cooled for 1 hr at 40. The crystals were removed, washed with hexane, funnel dried, the melting point determined, and the material recrystallized again and again until a constant melting point of 1240 (dec) was reached. In each case the crystals were definite yellow, transparent, short needles in somewhat fan-shaped clusters. The pure

**TABLE IX**

**DATA FOR FRACTIONAL CRYSTALLIZATION OF ISO-I**

<table>
<thead>
<tr>
<th>Initial amt.</th>
<th>#&lt;sup&gt;a&lt;/sup&gt;</th>
<th>p-Dioxane (ml)</th>
<th>Hexane (ml)</th>
<th>Amt. ReX&lt;sup&gt;a&lt;/sup&gt; (mg)</th>
<th>MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso-I (mg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>1st</td>
<td>10</td>
<td>30</td>
<td>337</td>
<td>95°</td>
</tr>
<tr>
<td>(337)</td>
<td>2nd</td>
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<td>15</td>
<td>252</td>
<td>105°</td>
</tr>
<tr>
<td>(252)</td>
<td>3rd</td>
<td>5</td>
<td>15</td>
<td>197</td>
<td>113°</td>
</tr>
<tr>
<td>(197)</td>
<td>4th</td>
<td>4</td>
<td>11</td>
<td>161</td>
<td>118°</td>
</tr>
<tr>
<td>(161)</td>
<td>5th</td>
<td>3</td>
<td>8½</td>
<td>140</td>
<td>121°</td>
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<td>3</td>
<td>10</td>
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<td>124°</td>
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<tr>
<td>(120)</td>
<td>7th</td>
<td>2</td>
<td>5</td>
<td>100</td>
<td>124°</td>
</tr>
</tbody>
</table>

<sup>a</sup>ReX = recrystallization or recrystallized.
material was dried at 56° using an Abderhalden pistol (P2O5) at 0.07 mm Hg for 7 hrs. (The P2O5 turned pink during this process.) NOTE: In every case the second crop was almost white and looked far better than the yellow first crop but in fact was much worse and, therefore, discarded while still in the mother liquor.

Structure. Crystallized I was identified as 2,3-dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether from the following evidence:

Anal. Calcd for C28H22Cl2N2O4: C, 64.60; H, 4.27; Cl, 13.64; N, 5.38. Found: C, 64.52; H, 4.00; Cl, 13.71; N, 5.40.

Ultraviolet spectrum (p-Dioxane, Figure 17): 
λ max 268 (44,200), 293 sh (16,600), 304 sh (11,630) and 325 nm (4,980).

Infrared spectrum (KBr, Figure 18):
764 (M), 782 (M), 805 (M), 820 (W), 842 (S), 935 (S), 972 (S, trans-CH=CH-), 1000 (S), 1033 (S), 1050 (S), 1087 (M), 1105 (M), 1119 (M), 1175 (S), 1206 sh (M), 1244 (S, aromatic C-O-C), 1274 sh (M), 1303 (S), 1356 (S), 1425 (S); 1450, 1504, 1568 and 1598 (M,S,W,S, aromatic), 1645 (W, C=C), 2222 (M, C≡N); 2818, 2910 and 2980 cm⁻¹ (M,M,M, aliphatic).
Nuclear magnetic resonance spectrum (CDCl₃, 3% w/v, Figure 19):

δ7.08 (q, 8, J_ab = 9.0 Hz, -C₆H₄-), 6.59 (d, 2, J_ab = 16.0 Hz, Hₐ), 6.29 (d of t, 2, Hₖ), 4.87 (d, 4, J_bx = 6.5 Hz, -CH₂) and 3.78 (s, 6, -OCH₃).

Mass spectrum:

The compound did not give a meaningful mass spectrum at 17, 20 or 70eV (port temperatures of 70-350°) apparently because of its negligible vapor pressure, decomposition at relatively low temperature and reactivity due to the allylic ether linkages.

5. Independent synthesis of 2,3-dichloro-5,6-dicyano-hydroquinone bis(1-p-anisy1propenyl) ether.

Preparation of p-methoxycinnamyl chloride. See Section D-1, p. 72.

Preparation of the disodium salt of 2,3-dichloro-5,6-dicyanohydroquinone. Forty grams of crude DDHQ was dissolved in 350 ml of Technical grade acetone (solution almost saturated) giving a black solution due to impurities adsorbed by DDHQ. Next 13.7 g of sodium hydroxide (0.2 g less than required) was dissolved in 100 ml of water and the resulting 3.4 N solution added with swirling to the acetone solution of DDHQ. The yellow salt formed immediately. After 10 min the solution was added to 400 ml of Technical acetone, and the salt
Figure 17. Left: UV Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (I) in p-Dioxane.
Right: UV Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (Syn-I) in p-Dioxane.
Figure 18. Top: IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (1).
Bottom: IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (Syn-1).
Figure 19. Top: NMR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (I) in CDCl₃.
Bottom: NMR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisylpropenyl) ether (Syn-I) in CDCl₃.
was partially dried in an oven (120°C, slowly) to remove most of the water of hydration; final drying was accomplished in a vacuum desiccator (0.15 mm Hg, 8 hr). This gave 34 g of extremely hygroscopic, granular product.

**Synthesis.** One gram of p-methoxycinnamyl chloride (5.5 mmol) was dissolved in 125 ml of benzene giving a colorless solution which stood overnight in some cases without change. A 0.75 g portion of the disodium salt of DDHQ (2.75 mmol) dissolved slowly in 25 ml of water in a 250 ml 3-necked round bottom flask, equipped with a thermometer and condenser, giving an intense yellow solution. To this was added 25 ml of p-dioxane which resulted in some degassing and imparted an orange cast to the solution. Addition of the benzene solution of p-methoxycinnamyl chloride to this mixture gave an overall bright yellow, two-phase suspension (solvent ratio 5:1:1, benzene/dioxane/water), which dissipated on heating at 60 ± 1°C for 20 minutes. Cooling the reaction mixture to room temperature in a water bath left a turbid orange organic phase and a turbid red aqueous phase. Phase separation was followed by back extraction of the aqueous phase once with a 25/25 ml benzene/p-dioxane solution, the extract being combined with the benzene phase. This in turn was extracted once with a 25/25 ml
dioxane/water solution and 4 times with 50 ml portions of water (these extracts were shown to contain only trace amounts of Cl~ and were discarded). Drying over magnesium sulfate left a bright, golden-yellow solution which on solvent removal in vacuo gave an orange paste. Addition of 25 ml of chilled methanol (10⁰) to this gave a slurry of crude I in methanol, containing soluble polymeric material and solvolysis products, which was separated by filtration through a coarse cintered glass funnel, washed with cold methanol, and dried under vacuum in a bell jar. Yield of Syn-I: 0.59 g (40%).

Workup of the filtrate as per Section C-4, p. 52 gave 0.1 g of DDHQ and 0.13 g of methyl ethers; methanolysis thus consumed approximately 4% of crude Syn-I.

Acidification of the aqueous phase (above) with nitric acid destroyed the color immediately; on standing, very fine, short needles of DDHQ (30 mg) crystallized from the solution. Silver nitrate (0.5 M) addition to the filtrate gave a white precipitate of silver chloride which yellowed on addition of excess reagent. The yield was 0.6 g which corresponded to 0.25 g (78%) as sodium chloride.

Crude Syn-I was purified in the same manner as Iso-I with the exception that the p-dioxane/hexane ratio was closer to 1:2 than 1:3. Table X lists the pertinent information.
### TABLE X
DATA FOR FRACTIONAL CRYSTALLIZATION OF SYN-I

<table>
<thead>
<tr>
<th>Initial amt. Syn-I (mg)</th>
<th>#a ReX</th>
<th>p-Dioxane (ml)</th>
<th>Hexane (ml)</th>
<th>Amt. ReXa (mg)</th>
<th>MP</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1st</td>
<td>2</td>
<td>3</td>
<td>62</td>
<td>119°</td>
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<tr>
<td>(62)</td>
<td>2nd</td>
<td>1</td>
<td>1 ½</td>
<td>48</td>
<td>122°</td>
</tr>
<tr>
<td>(48)</td>
<td>3rd</td>
<td>1</td>
<td>2</td>
<td>35</td>
<td>124°</td>
</tr>
<tr>
<td>(35)</td>
<td>4th</td>
<td>½</td>
<td>1</td>
<td>24</td>
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<tr>
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<td>1st</td>
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<td>116°</td>
</tr>
<tr>
<td>(222)</td>
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<td>4</td>
<td>5</td>
<td>140</td>
<td>122°</td>
</tr>
<tr>
<td>(140)</td>
<td>3rd</td>
<td>3</td>
<td>5</td>
<td>102</td>
<td>124°</td>
</tr>
</tbody>
</table>

a ReX = recrystallization and recrystallized.

Physical and spectral data given below were identical to that obtained for Iso-I and enabled identification of Syn-I as 2,3-dichloro-5,6-dicyanohydroquinone bis(1-\(\text{p}\)-anisylpropenyl) ether.

Anal. Calcd for \(\text{C}_{28}\text{H}_{22}\text{Cl}_{2}\text{N}_{2}\text{O}_{4}\): C, 64.60; H, 4.27; Cl, 13.64; N, 5.38. Found: C, 64.52; H, 4.04; Cl, 13.63; N, 5.45.

Ultraviolet spectrum (\(\text{p}\)-Dioxane, Figure 17):

\(\lambda_{\text{max}}\) 268 (45,500), 294 sh (17,380), 304 sh (12,040) and 324 nm (5,180).
Infrared spectrum (KBr, Figure 18):
764 (M), 873 (M), 805 (M), 820 (W), 842 (S),
934 (S), 971 (S, trans-Ch=Ch-), 1000 (S), 1030 (S),
1051 (S), 1086 (M), 1105 (M), 1120 (M), 1176 (S),
1245 (S, aromatic C-O-C), 1275 sh (M), 1302 (S),
1358 (S), 1425 (S); 1450, 1505, 1570 and 1600
(M, S, W, S, aromatic), 1646 (M, C=C), 2222 (M, C≡N);
2818, 2915, and 2975 cm⁻¹ (M, M, M, aliphatic).

Nuclear magnetic resonance spectrum (CDCl₃, 3% w/v, Figure 19):
δ7.08 (q, 8, Jₐₙ = 9.0 Hz, -C₆H₄⁻), 6.59 (d, 1,
Jₐₙ = 16.0 Hz, Hₐ), 6.29 (d of t, 2, Hₐ), 4.87
(d, 4, Jₜₓ = 6.5 Hz, -CH₂) and 3.78 (s, 6, -OCH₃).

Mass spectrum:
As in the case of 1so-I the compound did not give a meaningful mass spectrum.

6. Electron paramagnetic resonance studies of the reaction.
Detection of 2,3-dichloro-5,6-dicyanoquinone (DDQ).
A 0.0068 g portion of DDQ and 0.0069 g of DDHQ were each dissolved in 15 ml of solvent so that when mixed 10⁻³ M solutions resulted in both components. Three solvents were used: benzene (DDQ solution yellow, DDHQ solution turbid white), tetrahydrofuran (DDQ solution yellow, DDHQ solution colorless), and N,N-dimethyl-formamide
(DDQ solution orange-green, DDHQ solution yellow). In each case the solutions were mixed and placed directly into a quartz cell just prior to scanning the spectrum. In every case DDSQ was detected (Figure 56 and 57) although weakly in benzene. The field was calibrated with 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl and diphenyldipicrylhydrazyl (DPPH) was used as a g value standard \((g = 2.0036 \text{ MHz/gauss})\). This enabled calculation of g values for DDSQ: \(g_{\text{benzene}} = 2.0054; g_{\text{DMF}} = 2.0048\).

In a related experiment a \(5 \times 10^{-3} \text{ M}\) solution of DDHQ in tetrahydrofuran was prepared and scanned as above. Again DDSQ was detected but, in addition a weak triplet, superimposed on the OOSQ signal, also appeared (Figure 58).

In the reaction of interest a 0.0068 g portion of DDQ and 4.47 μl of anethole were each dissolved in 15 ml of benzene and portions of the resultant solutions placed into the separate reservoirs of a two-component flow system. (This consisted of two vertical 5 ml glass-tube reservoirs attached to two horizontal 5 cc syringes via two two-way valves which enabled solution to be drawn into the syringes and then ejected through the nozzle into a quartz Y connector attached to the bottom of a quartz EPR cell already positioned in the probe.) Equal volumes of solution were drawn into the syringes and then
injected into the cell, mixing occurring instantly. Flow rate about 1 ml/sec. The field, previously tuned to the DDSQ signal, was rapidly scanned at the moment of injection and more slowly thereafter. A weak triplet superimposed on the DDSQ signal was observed for this $10^{-3}$ M solution (Figure 58). It did not increase with time or with increasing concentration ($10^{-2}$ M and $10^{-1}$ M solutions were also run).

7. Description -- 1:2 Mole Reaction.

*Synthesis of p-methoxycinnamaldehyde (XI).* A 5.67 g portion of DDQ (25 mmol) was dissolved in 230 ml of benzene in a 500 ml Erlenmeyer flask. A solution of 1.86 ml of anethole (12.5 mmol) in 20 ml of benzene was added to this solution with swirling in one portion.

On contact, molecular complex formation produced a black solution which began to lighten in 5 sec. The reaction proceeded for 1 hr (stirred magnetically) after which vacuum filtration separated 4.3 g (75%) of purple DDHQ which became light brown on drying. Treatment of the orange-brown filtrate with 100 ml of water and then with an aqueous sodium borohydride solution (0.5 g in 50 ml water) gave immediate and vigorous reaction with much gas evolution and DDHQ sodium salt formation. Completion of the reaction was signaled by a brownish to yellow color change in the reaction mixture. Acidification
of the aqueous phase, following phase separation, precipitated the remaining DDHQ in the reaction. The organic phase was extracted 4 times with 50 ml portions of water, dried over magnesium sulfate, concentrated to about 15 ml and separated chromatographically on a silica gel column (1.7 x 38 cm, benzene slurry) with benzene as initial eluent. Fraction collecting commenced when the leading band had traversed one-half of the column. The developed chromatogram displayed 3 partially overlapping bands—a leading narrow, red-orange band at the bottom of the column (Band 1) followed by a broad yellow band (Band 2) in turned followed by a reddish-brown band at the column top (Band 3). Fraction 1: 40 ml of colorless eluent preceding Band 1; eluent switched to CHCl₃ at this point. Fraction 2: next 10 ml of orange eluent (Band 1). Fraction 3: next 175 ml of yellow eluent (trailing edge of Band 1 + Band 2). Band 3 and remaining materials on the column are polymeric in nature and were discarded. Solvent evaporation from the first two fractions gave 30 mg of a thick, foul-smelling, yellow liquid (benzene impurities) and 60 mg of a reddish liquid respectively. Fraction 3 gave 0.93 g (47%) of p-methoxycinnamaldehyde separating as an orange liquid which crystallized on standing. The crude material was conveniently purified by sublimation (0.1 mm Hg, 50°) to a white solid, mp 58-59° (lit. 71 59°).
Ultraviolet spectrum (p-Dioxane, Figure 20):

$\lambda_{\text{max}}$ 314 nm (22,700).

Infrared spectrum (Figure 21):

639 (W), 710 (W), 756 (W), 788 (M), 820 (M), 839 (S, para-sub. aromatic), 945 (W), 968 (S, trans-CH=CH-), 1035 (S), 1110 (M), 1126 (S), 1160 (M), 1176 (S), 1215 (M), 1245 (S, aromatic C-O-C), 1282 (M), 1305 (M), 1390 (W), 1426 sh (M), 1440 (M); 1457, 1505, 1570 and 1594 (M,S,M,S, aromatic), 1670 (S, C=O); 2718 and 2818 (W,M, aldehyde C-H) and 2910 cm$^{-1}$ (M, aliphatic).

Nuclear magnetic resonance spectrum (CCl$_4$, 15% w/v, Figure 22):

69.71 (d, 1, $H_c$), 7.28 (d, 1, $J_{ab} = 15.5$ Hz, $H_a$), 714 (q, 4, $J_{ab} = 9.0$ Hz, $-C_6H_4$), 6.48 (d of d, 1, $J_{bc} = 7.5$ Hz, $H_b$) and 3.80 (s, 3, $-OCH_3$).

Mass spectrum (70eV, Figure 23):

m/e 162 (M$^+$, base).

Effect of water on yield of p-methoxycinnamaldehyde (XI).

A 2.84 g portion of DDQ (12.5 mmol) was dissolved in 230 ml of benzene and 1 ml of water added to the resulting red solution. A solution of 0.93 ml of anethole (6.25 mmol) in 20 ml of benzene was added to this heterogeneous
solution, with swirling, in one portion. On contact, molecular complex formation produced a black solution which began to lighten in 5 sec. The reaction proceeded for 1 hr (stirred magnetically) after which filtration separated 2.07 g (72%) of tan DDHQ. The reaction was allowed to continue by heating (500') the now dark brown-yellow filtrate for 1 hr while stirring.

Filtration at the end of this time gave an additional 0.37 g (13%) of DDHQ and an orange solution. The latter was treated with 0.4 ml of anethole (excess) for 15 min to remove unreacted DDQ. This gave an extra 0.13 g of DDHQ (mint-green), corresponding to approximately 1 mmol of unreacted DDQ. The bright yellow filtrate was concentrated to about 20 ml and separated chromatographically as described above. Fraction 3 gave 0.79 g (78%) of p-methoxycinnamaldehyde.

Synthesis of p-methoxycinnamaldehyde-18O. The reaction with water described above was repeated using 0.905 g of 18O-water (20% 18O, 2.8% D, Bio-Rad laboratories). Corresponding yields of DDHQ were 2.15 g (75%), 0.3 g (10.5%) and 0.11 g (equal to about 1 mmol of unreacted DDQ). Fraction 3 gave 0.86 g (85%) of p-methoxycinnamaldehyde which was sublimed and subjected to mass spectral analysis. The spectrum revealed that 18O incorporation had occurred and that the material was 18.8% labelled (Figure 23).
Figure 20. Left: UV Spectrum of \( \text{B-Methoxycinnamaldehyde} \) (XII) in \( \text{Dioxane} \).
Right: UV Spectrum of \( \text{B-Methoxycinnamyl chloride} \) in \( \text{Cyclohexane} \).
Figure 21. Top: IR Spectrum of p-Methoxycinnamaldehyde (X1).
Bottom: IR Spectrum of p-Methoxycinnamyl chloride.
Figure 22. Top: NMR Spectrum of p-Methoxycinnamaldehyde (XI) in CCl₄.
Bottom: NMR Spectrum of p-Methoxycinnamyl chloride in CCl₄.
Figure 23. Top: 70 eV Mass Spectrum of p-Methoxycinnamaldehyde (X1).
Bottom: 70 eV Mass Spectrum of p-Methoxycinnamaldehyde-18O.
D. REACTIVITY OF 2,3-DICHLORO-5,6-DICYANOHYDROQUINONE BIS-(1-p-ANISYLPROPENYL) ETHER

1. Cleavage with hydrochloric acid.

Synthesis of p-methoxycinnamyl chloride. Working rapidly, the yellow benzene solution of I (Section C-2, p. 43) was treated with 10 ml of 6 N hydrochloric acid and then 40 ml of conc hydrochloric acid and stirred vigorously for \( \frac{1}{2} \) hr. As DDHQ formed, a murky tan suspension developed, making normal phase separation impossible. Consequently, 110 ml of 6N sodium hydroxide was slowly added to the suspension with ice-bath cooling until the separating aqueous phase became completely yellow. (Excess base was avoided, as it forced the sodium salt of DDHQ from solution.) Phase separation was now straightforward. Acidification (HCl) of the aqueous phase gave 2.56 g (45%) of DDHQ. The organic phase was extracted until neutral (2 x 50 ml water), dried over magnesium sulfate, and the solvent removed. The resultant red liquid was triturated 3 times with 50 ml of hexane and then twice with 25 ml of warm hexane (40\(^\circ\)); the brownish residue remaining was discarded. Solvent removal from the yellow hexane solution left 2.36 g of crude yellow-white p-methoxycinnamyl chloride which on purification by sublimation (0.1 mm Hg, 50\(^\circ\), 8 hr) gave 1.73 g (38%) of the pure white compound, mp 73.5-74.5\(^\circ\).
(lit. 72 71.5-73°). NOTE: The compound was quite unstable, decomposing to a greenish polymeric material with expulsion of hydrogen chloride even when stored in the dark in a desiccator. Accelerated decomposition occurred in the presence of light. The compound was thus stored a maximum of 1 day and usually prepared as needed; it was stored in benzene solution for longer time periods in some cases.

Anal. Calcd for C₁₀H₁₁ClO: C, 64.7; H, 6.1; Cl, 19.2. Found: C, 64.8; H, 6.1; Cl, 18.1.

Ultraviolet spectrum (Cyclohexane, Figure 20):

λ_{max} 222 sh (8,200), 242 sh (4,600), 247 sh (7,450), 253 sh (11,700), 259.5 sh (16,400), 268 (20,400), 293 sh (6,400) and 304 nm (3,500).

Infrared spectrum (KBr, Figure 21):

654 (S, C-Cl), 719 (W), 753 (W), 808 (S), 834 (S, parasub. aromatic), 858 (W), 919 (W), 943 (W), 961 (S), 972 (S, trans-CH=CH-), 1010 (M), 1032 (S), 1080 (M), 1114 (M), 1158 (M), 1177 (S), 1245 (S, aromatic C-O-C), 1286 (S), 1312 (M), 1416 (M), 1440 (H); 1466, 1510, 1572 and 1605 (H, S, H, H, aromatic), 1645 (M, C=C), 1895 (W), 2045 (W); 2832 and 2940 (M, M, aliphatic) and 3018 cm⁻¹ (M, aromatic C-H).
Nuclear magnetic resonance spectrum (CCl$_4$, 9% w/v, Figure 22):

$\delta$ 6.99 (q, 4, $J_{ab} = 9.0$ Hz, -C$_6$H$_4$-), 6.50 (d, 1, $J_{ab} = 15.5$ Hz, H$_a$), 6.08 (d of t, 1, H$_b$), 4.11 (d, 2, $J_{bx} = 6.5$ Hz, -CH$_2$) and 3.72 (s, 3, -OCH$_3$).

Mass spectrum (70eV, Figure 26):

m/e 182 ($M^+$), 147 (base).

Hydrogenation and solvolysis of p-methoxycinnamyl chloride.

Hydrogenation of 0.56 g of p-methoxycinnamyl chloride in methanol at 29°, using 0.15 g of 10% Palladium on carbon and hydrogen at 1 atm (Parr hydrogenator), resulted in hydrogen uptake at 2 ml/min for 10 min and 1 ml/15 min for 15 min. The reaction stopped completely after 25 min. The catalyst was removed by vacuum filtration, and methanol evaporated from the faintly yellow filtrate. Vacuum distillation of the resulting yellow liquid (short path, 3.5 mm Hg, pot temperature of 150°) gave 0.20 g (45%) of a colorless liquid at 90-100° which glpc revealed to be essentially one component (98%). Fractional distillation gave a pure sample for spectral data which characterized the compound as dihydroanethole.
Infrared spectrum (Figure 24):

696 (M), 741 (M), 788 (M), 810 (S), 836 (S, parasub. aromatic), 865 (W), 884 (W), 930 (W), 955 (W), 1038 (S), 1073 (M), 1096 sh (M), 1119 (S), 1178 (S), 1245 (S, aromatic C-O-C), 1298 (S), 1337 (W), 1380 (M), 1440 sh (S); 1460, 1510, 1583 and 1610 (S,S,M,S, aromatic), 1640 (W), 1705 (W), 1876 (W), 1985 (W), 2055 (W), 2780 sh (W), 2840 and 2900 cm\(^{-1}\) (S,S, aliphatic C-H).

Nuclear magnetic resonance spectrum (CCl\(_4\), 13\% w/v, Figure 25):

\[ \delta 6.85 \text{ (q, 4, } f_{ab} = 9.0 \text{ Hz, } -C_6H_4-), \delta 3.70 \text{ (s, 3, } -OCH}_3\), \delta 2.50 \text{ (t, 2, } J = 7.5 \text{ Hz, } -CH_2-CH_2), \delta 1.52 \text{ (sp, 2, } -CH_2CH_3) \text{ and } \delta 0.90 \text{ (t, 3, } J = 7.5 \text{ Hz, } -CH_3\).

Mass spectrum (70eV, Figure 26):

m/e 150 (M\(^+\)) and 121 (base).

A 1.64 g (9.0 mmol) portion of \(p\)-methoxycinnamyl chloride was solvolyzed with 25 ml of absolute ethanol and 1 ml of pyridine under reflux for 1 hr. Solvent removal left a whitish paste, trituration of which with ether separated the white, extremely hygroscopic pyridine hydrochloride. Evaporation of the ether left a yellow liquid which was taken up in 25 ml of chloroform, extracted with water (3 x 20 ml), returned as a yellow
Figure 24. Top: IR Spectrum of p-Methoxy-n-propylbenzene (Dihydroanethole).
Bottom: IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (Solid III).
Figure 25. NMR Spectrum of \( p \)-Methoxy-\( n \)-propylbenzene (Dihydroanethole) in \( \text{CCl}_4 \).
Figure 26. Top: 70 eV Mass Spectrum of p-Methoxycinnamyl chloride.
Bottom: 70 eV Mass Spectrum of p-Methoxy-n-propylbenzene (Dihydroanethole).
liquid after evaporation of the chloroform, and then vacuum distilled (short path, 0.1 mm Hg, pot temperature 140°). At 57-75° 0.96 g (56%) of p-methoxycinnamyl ethyl ether distilled--glpc showed it to be pure. Identification was based on comparison of the infrared spectrum (Figure 27) with that of authentic material (Section D-3, p. 83).

2. Oxidation by DDQ.

Synthesis of p-methoxycinnamaldehyde. A solution of 1.0 g of crude I (1.92 mmol) in 100 ml of benzene was filtered to remove 26 mg of trace DDHQ. The resultant pale yellow solution was added to a solution of 0.87 g of DDQ (3.84 mmol) in 20 ml of benzene. Molecular complex formation occurred as before, with DDHQ visible in solution in 2 min. After 2 hrs 0.9 g of purple solid was removed by filtration, leaving an orange filtrate which on solvent evaporation again darkened as the molecular complex reformed. The excess DDQ thus indicated was removed by addition of 0.3 ml of anethole which gave 0.12 g of DDHQ on reaction. The now bright yellow filtrate was concentrated to about 10 ml and separated chromatographically as described in Section C-7, p. 65. Fraction 1 gave 0.1 g of unreacted anethole, fraction 2 a trace amount of reddish resin, and fraction 3 p-methoxycinnamaldehyde (0.4 g). The aldehyde was purified by sublimation and
identified from a mixed melting point (58-59°) and comparison of spectral data with that for authentic material (Section C-7, p. 65). The yield of products and the amount of unreacted DDQ (1.06 mmol) indicated that the degree of reaction was 73%.

The purple solid was purified in the same manner as was DDHQ (Section C-2, p. 43), mp = 280° (dec).

**Anal.** Calcd for C₈H₂N₂Cl₂O₂: C, 41.95; H, 0.88; N, 12.23; Cl, 30.96. Found: C, 42.12; H, 0.96; N, 12.11; Cl, 31.19.

Ultraviolet spectrum (Methanol, Figure 28):

\[ \lambda_{\text{max}} 247 (19,100), 267 \text{sh (6,500), and 395 nm (7,460)}. \]

Infrared spectrum (KBr, Figure 24):

688 (W), 746 (M), 775 (M), 792 (W), 888 (S),
897 sh (S), 998 (W), 1075 (S), 1190 (S, C=O stretch),
1246 (S), 1274 (S), 1355 (M), 1445 (S, O-H bend),
1505 (W), 1567 (M), 2238 (S, C≡N) and 3205 cm⁻¹
(S, O-H stretch).

Mass spectrum (70eV, Figure 16):

m/e 228 (M⁺, base).

Final verification of this solid as DDHQ came from the diacetate derivative prepared as already described in Section C-2, p. 49. Mp 182-183° (lit. 68 181-182°).
Figure 27. IR Spectrum of p-Methoxycinnamyl ethyl ether (III).
Figure 28. UV Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (Solid III) in Methanol.
3. Solvolysis.

a. Synthesis of 1-\(\text{p}\)-anisylallyl ethyl ether (II) and \(\text{p}\)-methoxycinnamyl ethyl ether (III).

**Procedure.** To a benzene solution of I (Section C-2, p. 43) was added 50 ml of absolute ethanol and the mixture refluxed for \(\frac{1}{4}\) hr. At the end of this time the solvents were removed in vacuo and 100 ml of benzene added, precipitating 2.65 g (93%) of DDHQ. The red filtrate was concentrated to approximately 10 ml and separated on a Florisil column (1.7 x 38 cm, benzene) with chloroform as eluent. Polymeric and residual hydroquinone materials were retained by the column as a red band separated. Elution continued until this band was off of the column. Chloroform evaporation and vacuum distillation (short path) of the resultant red liquid at 0.3 mm Hg and 65-75\(^\circ\) gave 3.44 g (72%) of a pale yellow liquid which gcpc showed to be a 17:1 mixture of II and III. Separation was accomplished on a silica gel column (1.7 x 39 cm, benzene) with benzene as eluent, and fraction cutting at 30 ml intervals beginning from the moment all of the sample was on the column. Fractions 5-13 contained pure II, bp 245-247\(^\circ\).
Ultraviolet spectrum (Cyclohexane, Figure 29):
\[ \lambda_{\text{max}} 228 (9,300), 246 (1,250), 252 (1,600), \\
258 (2,150), 268 (1,650), 274 (2,650), 281 (2,200) \\
\text{and } 288 \text{ nm (970).} \]

Infrared spectrum (Figure 30):
783 (W), 813 sh (M), 831 (S, parasub. aromatic),
852 sh (M), 892 (W); 927 and 995 (M,M, -CH=CH₂),
1038 (S), 1090 (S), 1111 (S), 1176 (S), 1203 (W),
1245 (S, aromatic C-O-C), 1300 (M), 1335 (W),
1370 (W), 1395 (W), 1418 (W), 1443 (M); 1465,
1510, 1586 and 1610 (M,S,M,S, aromatic), 1642
(W, C=C); 2858 and 2960 (M,M, aliphatic C-H) and
3050 cm⁻¹ (W, aromatic C-H).

Nuclear magnetic resonance spectrum (CCl₄, 5% w/v,
Figure 31):
66.92 (q, 4, \( J_{ab} = 9.0 \text{ Hz, } -C₆H₄⁻ \)), 5.80 (q of d,
1, \( J_{ab} = 17.0 \text{ Hz, } J_{ac} = 10.0 \text{ Hz, } H_a \)), 5.10 (d of q,
1, \( J_{bc} = 2.0 \text{ Hz, } J_{bd} = 1.3 \text{ Hz, } H_b \)), 5.00 (d of q,
1, \( J_{cd} = 1.5 \text{ Hz, } H_c \)), 4.53 (d, 1, \( J_{ad} = 6.0 \text{ Hz, } H_d \)),
3.71 (s, 3, -OCH₃), 3.40 (d of q, 1, \( J_{ef} = 9.0 \text{ Hz, } H_e \)),
3.30 (d of q, 1, \( J_{eg} = J_{fg} = 7.0 \text{ Hz, } H_f \)) and
1.16 (t, 3, -CH₃).

Mass spectrum (70eV, Figure 33):
m/e 192 (M⁺) and 147 (base).
Fractions 16-21 contained pure III.

**Ultraviolet spectrum (Cyclohexane, Figure 29):**

\[ \lambda_{\text{max}} 253 \text{ sh (13,750)}, 259 \text{ sh (16,950)}, 263 (17,160), 288 (3,460) \text{ and } 304 \text{ nm (1,440)}. \]

**Infrared spectrum (Figure 30):**

758 (W), 784 (W), 801 (M), 842 (S, parasub. aromatic), 890 (W), 936 sh (W), 970 (S, trans -CH=CH-), 1074 sh (M), 1105 (S), 1123 (S), 1163 sh (M), 1176 (S), 1208 (M), 1250 (S, aromatic C-O-C), 1303 (M), 1355 (M), 1375 (M), 1420 (W), 1445 (M); 1460, 1510, 1578 and 1608 (M,S,M,S, aromatic), 1652 (W, C=C), 1690 (W, impurity); 2840 and 2960 cm\(^{-1}\) (M,M, aliphatic C-H).

**Nuclear magnetic resonance spectrum (CCl\(_4\), 5% w/v, Figure 32):**

8.695 (q, 4, \(J_{ab} = 9.0 \text{ Hz, -C}_6\text{H}_4^-\)), 6.39 (d, 1, \(J_{ab} = 16.0 \text{ Hz, } H_a\)), 6.01 (d of t, 1, \(J_{bx} = 5.5 \text{ Hz, } H_b\)), 3.98 (d of d, 2, \(H_{ax} = 1.0 \text{ Hz, } -\text{CH}_2(x)\)), 3.72 (s, 3, -OCH\(_3\)), 3.42 (q, 2, \(J = 7.0 \text{ Hz, } \text{CH}_2-\text{CH}_3\)) and 1.18 (t, 3, -CH\(_3\)).

**Mass spectrum (70eV, Figure 33):**

m/e 192 (M\(^+\)) and 135 (base).
Figure 29. Left: UV Spectrum of 1-p-Anisylalyl ethyl ether (II) in Cyclohexane. Right: UV Spectrum of p-Methoxycinnamyl ethyl ether (III) in Cyclohexane.
Figure 30. Top: IR Spectrum of 1-\(p\)-Anisylallyl ethyl ether (II).
Bottom: IR Spectrum of \(p\)-Methoxycinnamyl ethyl ether (III).
Figure 31. NMR Spectrum of 1-p-Anisylallyl ethyl ether (II) in CCl₄.
Figure 32. NMR Spectrum of \( \alpha \)-Methoxycinnamyl ethyl ether (III) in \( \text{CCl}_4 \).
Figure 33. Top: 70 eV Mass Spectrum of 1-\textit{p}-Anisylallyl ethyl ether (II).

Material recovery from the chromatographic separation was 88%.

Isomerization of 1-p-anisylallyl ethyl ether (II) to p-methoxycinnamyl ethyl ether (III). One gram of (II) was placed in a 50 ml round-bottomed flask containing 20 ml of absolute ethanol and 5 ml of 0.1 M perchloric acid. The mixture was heated under reflux for 1 hr. At the end of this time most of the ethanol was removed in vacuo and the aqueous phase extracted 3 times with 15 ml portions of ether. The ether extracts were back-extracted with distilled water twice and dried over magnesium sulfate. Evaporation of the ether left a pale yellow liquid which distilled at 1.0 mm Hg and 75-78° giving pure (III) as verified from spectral data and glpc analysis.

Stability of 1-p-anisylallyl ethyl ether (II) and p-methoxycinnamyl ethyl ether (III) to the reaction conditions. A colorless solution of 1.06 g of (II) in 100 ml of benzene was added to a pale yellow solution of 1.00 g of DDHQ in 50 ml absolute ethanol in a 300 ml round-bottomed flask and the mixture refluxed for ½ hr. Evaporation of the solvents and readdition of benzene separated 0.93 g (93%) of unchanged DDHQ. Filtration workup gave a pale yellow liquid which distilled at 0.15 mm Hg and 53-58° to give 0.88 g of
unchanged (II) as verified by spectral data and glpc analysis. In like fashion (III) underwent no change when subjected to the same conditions.

b. Synthesis of 1-p-anisylallyl methyl ether (IV) and p-methoxycinnamyl methyl ether (V).

The methanolysis procedure was identical to that used for ethanolysis. The amount of DDHQ recovered was 2.70 g (95%) while the pale yellow distillate obtained at 0.3 mm Hg and 61-71° amounted to 3.10 g (70%). Glpc revealed a 13:1 mixture of IV and V which on separation gave pure IV, bp 239-240° and pure V. Spectral data for 1-p-anisylallyl methyl ether (IV):

**Ultraviolet spectrum (Cyclohexane, Figure 34):**

\[ \lambda_{max} 229 (11,200), 267 (2,550), 275 (2,550), \text{ and } 281 \text{ nm (2,100).} \]

**Infrared spectrum (Figure 35):**

783 (W), 813 sh (M), 830 (S, parasub. aromatic), 851 sh (M); 926 and 993 (S,M,-CH=CH₂), 1037 (S), 1088 (S), 1105 sh (S), 1140 (W), 1175 (S), 1205 (W), 1245 (S, aromatic C-O-C), 1302 (S), 1337 (W), 1415 (W), 1442 (M); 1462, 1508, 1585 and 1606 (M,S,M,S, aromatic), 1640 (W, C=C), 1690 (W, impurity); 2810, 2915 and 2968 sh (M,M,M, aliphatic C-H) and 3050 cm⁻¹ (W, aromatic C-H).
Nuclear magnetic resonance spectrum (CCl\textsubscript{4}, 16% w/v, Figure 36):
\begin{align*}
\delta & 6.96 (q, 4, J_{ab} = 9.0 \text{ Hz}, -C_6H_4), 5.86 (q \text{ of } d, \\
& 1, J_{ab} = 17.0 \text{ Hz}, J_{ac} = 9.5 \text{ Hz}, H_a), 5.12 (d \text{ of } q, \\
& 1, J_{bc} = 2.5 \text{ Hz}, J_{bd} = 1.3 \text{ Hz}, H_b), 5.06 (d \text{ of } q, \\
& 1, J_{cd} = 1.3 \text{ Hz}, H_c), 4.45 (d, 1, J_{ad} = 6.0 \text{ Hz}, H_d), \\
& 3.72 (s, 3, aryl-OCH\textsubscript{3}) \text{ and } 3.20 (s, 3, -OCH\textsubscript{3}).
\end{align*}

Mass spectrum (70eV, Figure 37):
\begin{align*}
m/e & 178 (M^{+}) \text{ and } 147 \text{ (base)}.
\end{align*}

Spectral data for p-methoxycinnamyl methyl ether (V):

Infrared spectrum (Figure 35):
\begin{align*}
756 & (W), 800 (M), 840 (M, \text{ parasub. aromatic}), 914 (W), 971 (M, \text{ trans-CH=CH-}), 1038 (S), 1070 sh (M), \\
1087 & sh (S), 1106(S), 1120 (S), 1153 (W), 1176 (S), \\
1208 & (W), 1246 (S, \text{ aromatic C-O-C}), 1303 (M), 1380 (W), 1420 (W), 1440 (M); 1462, 1508, 1578 \text{ and } 1605 \\
(M,S,W,S, \text{ aromatic}), 1646 (W, C=C); 2818 \text{ and } \\
2908 & \text{ cm}^{-1} (M,M, \text{ aliphatic C-H}).
\end{align*}

Nuclear magnetic resonance spectrum (CCl\textsubscript{4}, 15% w/v, Figure 36):
\begin{align*}
\delta & 6.96 (q, 4, J_{ab} = 9.0 \text{ Hz}, -C_6H_4), 6.42 (d, 1, \\
& J_{ab} = 16.0 \text{ Hz}, H_a), 6.01 (d \text{ of } t, 1, J_{bx} = 5.5 \text{ Hz}, \\
& H_b), 3.94 (d, 2, -CH\textsubscript{2}(x)), 3.72 (s, 3, aryl-OCH\textsubscript{3}), \\
& \text{ and } 3.21 (s, 3, -OCH\textsubscript{3}).
\end{align*}
c. Synthesis of l-\(p\)-anisylallyl-l-propyl ether (VI) and \(p\)-methoxy cinnamyl-l-propyl ether (VII).

Formation of these ethers was as for the ethanolysis case with the exception that the reflux time was increased to 1 hr. The DDHQ separated amounted to 2.66 g (94%); the pale yellow distillate obtained at 0.3 mm Hg and 65-70° to 2.30 g (45%). Glpc analysis revealed a 2:1 mixture of VI and VII which was separated as follows:

A 10 ml benzene solution of the ethers was chromatographed on a silica gel column (1.7 x 39 cm, benzene) by collecting thirty 30 ml fractions, beginning from the moment all of the solution was on the column. Eluents were 1:4 benzene/hexane initially and 100% benzene after fraction 18. Fractions 4-17 contained pure l-\(p\)-anisylallyl-l-propyl ether, bp 249°.

Ultraviolet spectrum (Cyclohexane, Figure 34):

\[ \lambda_{\text{max}} \] 228 (11,750), 248 (2,950), 254 (3,850), 260 (4,150), 267 (3,850), 274 (3,600), 281 (3,050) and 287 nm (1,150).

Infrared spectrum (Figure 38):

782 (W), 813 sh (M), 838 (S, parasub. aromatic), 855 sh (M); 925 and 995 (S,M,-CH=CH\(_2\)), 954 (W), 1038 (S), 1058 sh (S), 1111 (S), 1124 (S), 1145 (M), 1162 (M), 1174 (S), 1200 (W), 1245
Figure 34. Left: UV Spectrum of 1-\(\beta\)-Anisylallyl methyl ether (IV) in Cyclohexane.
Right: UV Spectrum of 1-\(\beta\)-Anisylallyl-\(i\)-propyl ether (VI) in Cyclohexane.
Figure 35. Top: IR Spectrum of 1-p-Anisylallyl methyl ether (IV).
Bottom: IR Spectrum of p-Methoxycinnamyl methyl ether (V).
Figure 36. Top: NMR Spectrum of \( \text{-p-Anisylallyl methyl ether (IV)} \) in \( \text{CCl}_4 \).
Bottom: NMR Spectrum of \( \text{-Methoxycinnamyl methyl ether (V)} \) in \( \text{CCl}_4 \).
Figure 37. Top: 70 eV Mass Spectrum of 1-α-Anisylallyl methyl ether (IV).  
Bottom: 70 eV Mass Spectrum of 1-α-Anisylallyl-i-propyl ether (VI).
(S, aromatic C-O-C), 1300 (M), 1330 (M), 1375 (M),
1380 sh (M), 1418 (W), 1444 (M); 1464, 1508,
1585 and 1608 (M,S,M,S, aromatic), 1640 (W, C=C),
1693 (M, impurity); 2832 and 2950 (M,S, aliphatic
C-H) and 3050 cm⁻¹ (W, aromatic C-H).

Nuclear magnetic resonance spectrum (CCl₄, 5% w/v,
Figure 39):
δ6.91 (q, 4, J_ab = 9.0 Hz, -C₆H₄-), 5.79 (q of d,
1, J_ab = 17.0 Hz, J_ac = 10.0 Hz, H_a), 5.08 (d of q,
1, J_bd = 1 Hz, H_b), 4.99 (d of q, 1, J_cd = 1 Hz,
H_c), 4.68 (d, 1, J_ad = 5.5 Hz, H_d), 3.72 (s, 3, -OCH₃),
3.55 (sp, 1, J_ef = J_eg = 6.0 Hz, H_e), 1.14 (d, 3,
-CH₃(f)) and 1.08 (d, 3, -CH₃(g)).

Mass spectrum (70eV, Figure 37):
m/e 206 (M⁺) and 135 (base).

Fractions 20-25 contained pure p-methoxycinnamyl-1-
propyl ether.

Infrared spectrum (Figure 38):
758 (W), 784 (M), 790 (M), 840 (S, parasub. aromatic),
852 sh (M), 906 (W), 923 (W), 936 (W), 970 (S, trans-
-CH=CH-), 1038 (S), 1058 (S), 1105 (M), 1126 (S),
1145 (S), 1176 (S), 1205 (W), 1246 (S, aromatic C-O-C),
1275 (M), 1304 (M), 1335 (M), 1370 (M), 1377 (M),
1418 (W), 1445 (M); 1465, 1509, 1575 and 1605 (M, S, W, S, aromatic), 1654 (W, C=C); 2830 and 2950 cm$^{-1}$ (M, M, aliphatic C-H).

Nuclear magnetic resonance spectrum (CCl$_4$, 10% w/v, Figure 39):

$\delta$ 6.94 (q, 4, $J_{ab} = 9.0$ Hz, $-C_6H_4^{-}$), 6.39 (d, 1, $J_{ab} = 16.0$ Hz, $H_a$), 5.99 (d of t, 1, $J_{bc} = 5.5$ Hz, $H_b$), 3.96 (d of d, 2, $J_{ac} = 1.0$ Hz, $-CH_2(c)$), 3.70 (s, 3, $-OCH_3$), 3.55 (sp, 1, $J_{de} = 6.0$ Hz, $H_d$) and 1.14 (d, 6, $-CH_3$).

d. Synthesis of 1-p-anisylallyl-\textit{t}-butyl ether (VIII) and \textit{p}-methoxycinnamyl-\textit{t}-butyl ether (IX).

Formation of these ethers was as for the ethanolation case with two exceptions. The reflux time was 3 hrs after which 1.96 g (69%) of DDHQ was separated, and 1.30 g (24%) of yellow distillate obtained at 0.3 mm Hg and 60-81$^\circ$. Glpc analysis revealed a mixture of 5 components (labelled A, B, C, D and E in order of increasing retention times of 2.7, 4.4, 5.8, 8.2 and 15.3 min respectively) of which C and E proved to be VIII and IX respectively. Separation was accomplished by a revised chromatographic procedure as follows. A benzene solution of the mixture was spotted on a silica gel column (1.7 x 110 cm, benzene) and sixty 30 ml fractions collected after an initial 125 ml of benzene had eluted.
Figure 38. Top: IR Spectrum of 1-p-Anisylallyl-1-propyl ether (VI).
Bottom: IR Spectrum of p-Methoxycinnamyl-1-propyl ether (VII).
Figure 39. Top: NMR Spectrum of 1-β-Anisylallyl-i-propyl ether (VI) in CCl₄.
Bottom: NMR Spectrum of β-Methoxycinnamyl-i-propyl ether (VII) in CCl₄.
Workup showed that fractions 1-8 contained VIII (1.9%), fractions 12-17 compound IX (17%) mp 44-45°, and fractions 46-54 p-methoxycinnamaldehyde (2.5%). The other fractions were various mixtures of two or more of the components. Spectral data for l-p-anisylallyl-t-butyl ether (VIII):

Infrared spectrum (Figure 40):
652 (M), 753 (W), 760 (W), 786 (M), 810 (S),
828 (S, parasub. aromatic), 861 (M), 900 (M);
922 and 993 (S,S,-CH=CH\textsubscript{2}), 1022 (S), 1040 (S),
1062 (S), 1102 (S), 1122 (S), 1170 (S), 1194 (S),
1246 (S, aromatic C-O-C), 1300 (S); 1365 and 1390
(S,S, gem-dimethyl), 1414 (M), 1440 (S); 1460,
1508, 1585 and 1610 (S,S,M,S, aromatic), 1640
(M, C=C); 2818 sh and 2940 (M,S, aliphatic C-H)
and 3050 cm\textsuperscript{-1} (W, aromatic C-H).

Nuclear magnetic resonance spectrum (CCl\textsubscript{4}, 6% w/v, Figure 41):
δ6.91 (q, 4, J\textsubscript{ab} = 9.0 Hz, -C\textsubscript{6}H\textsubscript{4}−), 5.81 (q of d,
1, J\textsubscript{ab} = 16.0 Hz, H\textsubscript{a}), 5.03 (d of q, 1, H\textsubscript{b}),
4.90 (d of q, 1, J\textsubscript{ac} = 10.0 Hz, H\textsubscript{c}), 4.83 (d, 1,
J\textsubscript{ad} = 5.5 Hz, H\textsubscript{d}), 3.71 (s, 3, -OCH\textsubscript{3}) and
1.17 (s, 9, -CH\textsubscript{3}).

Mass spectrum (70eV, Figure 42):
m/e 220 (M\textsuperscript{+}) and 163 (base).
Spectral data for $p$-methoxycinnamyl-$t$-butyl ether (IX):

Infrared spectrum (Figure 40):

750 (W), 785 (M), 806 sh (M), 840 (s, parasub. aromatic), 886 (M), 971 (s, **trans**-CH=CH-), 1036 (s), 1065 (s), 1105 (s), 1118 (s), 1176 (s), 1196 (s), 1246 (s, aromatic C-O-C), 1275 sh (s), 1300 (s); 1246 and 1390 (s, M, gem-dimethyl), 1420 (M), 1440 (M); 1465, 1508, 1575 and 1605 (s, M, aromatic), 1672 (W, impurity); 2830 and 2940 (s, S, aliphatic C-H) and 3421 cm$^{-1}$ (M, water).

Nuclear magnetic resonance spectrum (CCl$_4$, 6% w/v, Figure 41):

$\delta$ 6.93 (q, 4, $J_{ab} = 9.0$ Hz, -C$_6$H$_4$-), 6.38 (d, 1, $J_{ab} = 16.0$ Hz, $H_a$), 5.98 (d of t, 1, $J_{bx} = 5.5$ Hz, $H_b$), 3.94 (d, 2, -CH$_2$(x)), 3.68 (s, 3, -OCH$_3$) and 1.20 (s, 9, -CH$_3$).

4. Attempted alkylation.

A 2.0 g portion of crude I was dissolved in 200 ml of warm benzene (slow process), 50 ml (excess) of redistilled anethole added, and the pale yellow solution refluxed for 1 hr. Within 2 min the solution had darkened to a deep yellow, was orange after 5 min and dark red at the end of the hour. No solid formed. Removal of the benzene left a dark liquid from which
everything volatile was removed by distillation at 0.2 mm Hg and 250°. The resulting intractable, black pot residue was discarded and the pale orange distillate redistilled at 0.2 mm Hg and 75-80° to give about 50 ml of unreacted anethole as determined by glpc analysis (one component) and infrared spectral data.

In a variation of the above procedure the benzene solution of I was treated with a second mole of anethole (3.72 ml) and stirred magnetically while slowly adding 10 ml portions of perchloric acid of gradually increasing strength. No visible change occurred with 10-40% acid. With 45% perchloric acid the solution darkened and in ½ hr was very dark red, indicative of anethole polymerization.

E. OXIDATION OF ESTRAGOLE BY DDQ

1. Description -- 1:1 Mole Reaction.

Identification of 2,3-dichloro-5,6-dicyanohydroquinone (DDHQ). In a typical run 5.67 g of DDQ (25 mmol) was dissolved in 230 ml of benzene in a 500 ml Erlenmeyer flask. A solution of 3.84 ml of estragole (25 mmol) in 20 ml of benzene was added to this solution with swirling in one portion. On contact the red quinone solution instantly turned intensely green (looks black) as the reactants formed a molecular complex--magnetic stirring was commenced immediately. Within 2 min some solid was
Figure 40. Top: IR Spectrum of 1-p-Anisylallyl-t-butyl ether (VIII).
Bottom: IR Spectrum of p-Methoxycinnamyl-t-butyl ether (IX).
Figure 41. Top: NMR Spectrum of 1-p-Anisylallyl-\(t\)-butyl ether (VIII) in CCl\(_4\).
Bottom: NMR Spectrum of \(p\)-Methoxycinnamyl-\(t\)-butyl ether (IX) in CCl\(_4\).
Figure 42. 70 eV Mass Spectrum of 1-p-Anisylallyl-\text{-}t\text{-}butyl ether (VIII).
visible in solution and after 1 hr filtration separated 4.15 g (72%) of purple solid which on purification and characterization proved to be DDHQ by comparison with an authentic sample of material obtained as described in Section C-2, p. 43.

Identification of 2,3-dichloro-5,6-dicyano-hydroquinone mono(1-p-anisylpropenyl) ether (X). The yellow-orange filtrate from above was stabilized by p-dioxane/water extraction (Section C-4, p. 52) and dried over magnesium sulfate. Solvent removal in vacuo left a sandy-orange paste which on readdition of about 30 ml of benzene produced a slurry, filtration of which gave 2.0 g (21%) of crude X. Purification was accomplished by reprecipitation from chloroform/hexane based on a solubility figure of 15 mg/ml. Thus addition of 150 ml of chloroform to the crude material produced a very turbid solution, filtration of which removed most of the major impurity, DDHQ. The chloroform was then removed and 60 ml readded giving a second slightly turbid solution. This was filtered to remove the remaining DDHQ and then treated with 600 ml of hexane while stirring vigorously. The off-white material which precipitated was separated by filtration and dried under vacuum (bell jar, 0.1 mm Hg, 4 hr). Recovery: 0.8 g (40%), mp 100° (dec).
Anal. Calcd for C₁₈H₁₂C₁₂N₂O₃: C, 57.80; H, 3.23; N, 7.50; Cl, 18.95. Found: C, 57.58; H, 3.18; N, 7.42; Cl, 18.91.

Ultraviolet spectrum (p-Dioxane, Figure 43):

\[ \lambda_{\text{max}} 267 (24,800), 292 \text{ sh } (6,550), 305 (4,700) \]
\[ 325 \text{ sh } (4,900) \text{ and } 340 \text{ nm } (5,850). \]

Infrared spectrum (KBr, Figure 44):

742 (W), 777 (W), 838 (M, parasub. aromatic), 893 (M), 928 (M), 968 (M, trans-\( \text{CH} = \text{CH} \)), 1000 (M), 1075 (M), 1174 (S), 1202 (S, C-O stretch), 1242 (S, aromatic C-O-C), 1274 sh (S), 1300 sh (M), 1328 (M), 1366 (M), 1414 (S, O-H bend); 1433, 1500, 1563 and 1595 (S,M,W,M, aromatic), 1640 sh (W, C=C), 2220 (M, -C=N); 2810 and 2900 (M,M, aliphatic C-H) and 3195 cm\(^{-1}\) (M, O-H stretch).

Nuclear magnetic resonance spectrum (DMSO-d₆, 5% w/v, Figure 45):

\[ \delta 7.14 \text{ (q, 4, } J_{\text{ab}} = 9.0 \text{ Hz, } -C_6H_4^-), 6.66 \text{ (d, 1, } J_{\text{ab}} = 16.0 \text{ Hz, } H_a), 6.32 \text{ (d of t, 1, } J_{\text{bx}} = 6.0 \text{ Hz, } H_B), 4.76 \text{ (d, 2, } -\text{CH}_2(x)) \text{ and } 3.75 \text{ (s, 3, } -\text{OCH}_3). \]

Ethanolysis of 2,3-dichloro-5,6-dicyanohydroquinone mono (1-p-anisylpropenyl) ether (X). A 1.33 g portion of crude X was dissolved in 200 ml of benzene and the
solution filtered to remove 0.31 g of DDHQ, leaving about 1.0 g (2.65 mmol) of X in solution. This was solvolyzed as previously described (Section D-3, p. 83). Products found were 0.33 g of DDHQ (54%) and an 11:1 mixture of 1-p-anisylallyl ethyl ether and p-methoxycinnamyl ethyl ether, 0.17 g (33%).

**Identification of p-methoxycinnamaldehyde (XI).** The red filtrate left after separation of X was concentrated to about 15 ml and separated chromatographically as previously described (Section C-7, p. 65). Solvent removal from the first two fractions gave 0.8 g (22%) of unreacted estragole, identified by comparison with an authentic sample, and a trace amount of reddish liquid, respectively. Fraction 3 gave 0.7 g (17%) of p-methoxycinnamaldehyde separating as an orange liquid which crystallized on standing. The crude material was conveniently purified by sublimation and identified by comparison with an authentic sample.

**Test for column oxidation of estragole.** A 0.55 g portion of estragole (glpc pure) was eluted with 150 ml of benzene from a 1.3 x 20 cm Florisil column. Solvent removal returned 0.53 g of estragole glpc pure. No p-methoxycinnamaldehyde was formed.
2. Description -- 1:2 Mole Reaction.

Normal reaction. In a typical experiment 5.67 g of DDQ (25 mmol) was dissolved in 230 ml of benzene in a 500 ml Erlenmeyer flask. A solution of 1.92 ml of estragole (12.5 mmol) in 20 ml of benzene was added to this with swirling, in one portion. On stirring magnetically, reaction proceeded as for the 1:1 mole ratio case except that the dark color persisted after 2 hrs. The unreacted DDQ thus indicated was removed by two alternative methods.

First, 4.83 g (84%) of DDHQ was removed by vacuum filtration and then estragole (0.5 ml) added to the dark filtrate. Disappearance of the dark solution color, leaving an orange-red solution, indicated completion of the reaction. The additional solid that formed was removed and the filtrate concentrated to about 15 ml and separated chromatographically as already described (Section C-7, p. 65). Fraction 3 gave 1.0 g (50%) of \( \text{p}-\text{methoxycinnamaldehyde} \).

A second method consisted of adding an aqueous sodium borohydride solution (1.0 g of NaBH\(_4\)/50 ml H\(_2\)O) directly to the initial filtrate following DDHQ removal. There was immediate and vigorous reaction with much gas evolution and sodium salt formation. Water (100 ml) was added to the reaction mixture during the reaction to keep the salt in solution. Completion of reaction was indicated by a solution color change of black to yellow.
Acidification of the aqueous phase, following phase separation, precipitated the remaining DDHQ from the reaction. The organic phase was extracted with water (4 x 50 ml), dried over magnesium sulfate, concentrated to about 15 ml, and separated chromatographically as described above. Again the yield of \( p \)-methoxycinnamaldehyde was 1.0 g (50%).

Effect of dropwise addition of reactants on the reaction.
A 5.67 g portion of DDQ (25 mmol) was dissolved in 100 ml of benzene and placed in a 100 ml pressure-equalized addition funnel. A 1.92 ml portion of estragole (12.5 mmol) was dissolved in 150 ml of benzene and placed in a 500 ml, 3-necked, round-bottomed flask equipped with a nitrogen inlet tube, addition funnel, condenser, and magnetic stirrer. The quinone solution was added to the stirred olefin solution at the initial rate of 3 ml/min. Addition required about 1 hr; the reaction proceeded an additional 2 hrs. Workup by addition of excess estragole was as described above (Section E-2, p. 112). The yield of \( p \)-methoxycinnamaldehyde was 0.4 g (20%).

The reaction was repeated this time adding the olefin dropwise to the quinone solution. Again the yield of \( p \)-methoxycinnamaldehyde was less than in other cases, 0.5 g (25%).
Effect of a nitrogen atmosphere on the reaction.

A 5.67 g portion of DDQ (25 mmol) was dissolved in 230 ml of benzene in a 500 ml round-bottomed flask. A solution of 1.92 ml of estragole (12.5 mmol) in 20 ml of benzene was added to this with swirling in one portion while the flask was being flushed with nitrogen. The flask was then sealed and the reaction allowed to proceed under the nitrogen atmosphere for 14 hr. Workup by addition of excess estragole was as above. Yield of $\beta$-methoxy-cinnamaldehyde: 1.0 g (50%).

Effect of $\beta$-dioxane as solvent on the reaction.

A 5.67 g portion of DDQ (25 mmol) was dissolved in 230 ml of $\beta$-dioxane in a 500 ml Erlenmeyer flask. Dissolution was faster than in benzene and gave a yellow-orange solution. A solution of 1.92 ml of estragole (12.5 mmol) in 20 ml of $\beta$-dioxane was added with swirling in one portion to the DDQ solution. On contact molecular complex formation imparted a black color to the solution. After 50 min the first small amount of solid was visible in the stirred gray-green solution. After 3 hrs the solution was entirely yellow but solid continued to precipitate. At the end of 23½ hr removal of 3.7 g (65%) of DDHQ left a yellow filtrate which on solvent evaporation gave an orange residue that separated an additional 1.0 g (17%) of DDHQ when taken up in benzene. The
red-orange filtrate was then extracted with aqueous sodium borohydride and worked up as already described (Section E-2, p. 112). Yield of \( p \)-methoxycinnamaldehyde: 0.9 g (45%).

**Effect of methylene chloride as solvent on the reaction.**

A 5.67 g portion of DDQ (25 mmol) was dissolved (very slowly) in 330 ml of methylene chloride. A solution of 1.92 ml of estragole (12.5 mmol) in 20 ml of methylene chloride was added to this in one portion. The light orange quinone solution instantly turned black as the reactants formed a molecular complex. Within 2 min the solution was dark green and some DDHQ was visible; after 30 min the DDHQ was purple and the solution brown-yellow. At the end of 22 hrs 4.7 g (82%) of DDHQ was removed but the yellow-brown solution color persisted, indicating unreacted DDQ. Removal of the methylene chloride and readdition of benzene separated an additional 0.2 g (3%) of DDHQ. The black filtrate was worked up as already described for the reaction in \( p \)-dioxane. Yield of \( p \)-methoxycinnamaldehyde: 0.9 g (45%).

3. Description -- 1:3 Mole Reaction.

An 8.51 g portion of DDQ (37.5 mmol) was dissolved in 280 ml of benzene in a 500 ml round-bottomed flask. A solution of 1.92 ml of estragole (12.5 mmol) in 20 ml of benzene was added to this in one portion. After
Figure 43. Left: UV Spectrum of 2,3-Dichloro-5,6-dicyanoquinone mono(1-p-anisylpropenyl) ether (X) in £-Dioxane.
Right: UV Spectrum of 2,3-Dichloro-5,6-dicyanoquinone monocinnamyl ether (XII) in p-Dioxane.
Figure 44. Top: IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone mono(1-p-anisylpropenyl) ether (X).
Bottom: IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone monocinnamyl ether (XII).
Figure 45. Top: NMR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone mono(1-β-anisylpropenyl) ether (X) in DMSO-d$_6$.
Bottom: NMR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone monocinnamyl ether (XII) in DMSO-d$_6$.
2 hrs, 4.86 g (85%) of DDHQ was removed, and the excess quinone present in the filtrate removed by reaction with sodium borohydride as described in Section E-2, p. 112. Workup of the resultant solution was as per Section E-2 also. Yield of \( \rho \)-methoxycinnamaldehyde: 1.2 g (60%).

F. POLYMERIZATION OF \( \rho \)-METHOXYSTYRENE BY DDQ

A solution of 1.68 ml of \( \rho \)-methoxystyrene (12.5 mmol) in 25 ml of benzene was added to a solution of 2.84 g of DDQ (12.5 mmol) in 100 ml of benzene, and the mixture stirred magnetically at room temperature. On contact, molecular complex formation produced a black solution which had not changed after 3 hrs. At the end of 20 hr, much sticky, purple polymer had settled to the bottom of the reaction vessel. Solvent evaporation from the solution gave only more polymer. Further analysis was not attempted.

G. OXIDATION OF \( \beta \)-METHYLSTYRENE BY DDQ

1. Description -- 1:1 Mole Reaction.

Identification of DDHQ. In a typical experiment a solution of 3.23 ml of \( \beta \)-methylstyrene (25 mmol) in 20 ml of benzene was added with swirling in one portion to a solution of 5.67 g of DDQ (25 mmol) in 230 ml of benzene. On contact a black molecular complex formed instantly and within 2 min DDHQ was visible in the magnetically stirred solution. After 20 hr 2.2 g (38%) of greenish solid, identified as DDHQ by comparison with
authentic material (Section C-2, p. 43), was separated by filtration, leaving a red solution which on concentration to about 20 ml forced crude XI from solution. Filtration and washing with benzene gave 2.2 g (25%) of pale green XI.

Identification of 2,3-dichloro-5,6-dicyanohydroquinone monocinnamyl ether XII. Crude XII was purified by reprecipitation from chloroform/hexane based on a solubility figure of 15 mg/ml. Thus, addition of 150 ml of chloroform to the crude material produced a turbid solution, filtration of which removed most of the major impurity, DDHQ. The chloroform was then evaporated and the minimum amount needed to affect solution readded (30 ml). The resulting solution was filtered to remove a remaining small amount of DDHQ, warmed to 40°C, taken to turbidity with about 45 ml of hexane, and cooled at 4°C for 1 hr. The material reprecipitated as an amorphous, light tan solid, mp 130°C (dec).

Anal. Calcd for C₁₇H₁₀Cl₂N₂O₂: C, 59.15; H, 2.92; N, 8.12; Cl, 20.52. Found*: C, 61.58; H, 3.23; N, 6.08; Cl, 19.96.

Ultraviolet spectrum (p-Dioxane, Figure 43):

\[ \lambda_{\text{max}} 254 \text{ (26,250), 284 sh (4,300), 292 (3,000), 302 (2,500), 326 sh (4,800) and 340 nm (6,050).} \]

*Analysis by C. F. Geiger.
Infrared spectrum (KBr, Figure 44):

692 and 750 (M,M, monosub. aromatic), 778 (M),
826 (W), 890 (M), 935 (S), 969 (M, trans-CH=CH-),
996 (M), 1028 (W), 1075 (M), 1111 (W), 1195
(S, C-O stretch), 1328 (S), 1372 (S), 1422 sh
(S, O-H bend), 1433 (S), 1488 (W), 1550 (W),
2227 (M, C=N), and 3245 cm⁻¹ (S, O-H stretch).

Nuclear magnetic resonance spectrum (DMSO-d₆, 5% w/v, Figure 45):

δ7.36 (m, 5, C₆H₅-), 6.76 (d, 1, Jₐb = 16.0 Hz,
Hₐ), 6.50 (d of t, 1, J₃₄ = 6.0 Hz, H₃) and
4.82 (d, 2, -CH₂).

Identification of cinnamaldehyde (XIV). The red
filtrate left after removal of XI I was concentrated to
about 20 ml and separated chromatographically on a
silica gel column (1.7 x 38 cm, benzene) with benzene
as initial eluent. Initial spotting was as a deep
red-black 8 cm band with a leading yellow edge.
Fraction collecting commenced as soon as the material
was on the column. The developed chromatogram displayed
3 partially overlapping bands, a leading yellow band
(Band 1) followed by a narrow orange band (Band 2) in
turn followed by a very broad red band (Band 3) extending
to the column top. Fraction 1: 60 ml of colorless
eluent preceeding Band 1, eluent switched to chloroform
at this point; fraction 2: next 60 ml of yellow eluent (Band 1); fraction 3: next 70 ml of pale orange eluent (Band 2); fraction 4: next 140 ml of pale yellow eluent (material between Bands 2 and 3); fraction 5: next 125 ml of red-orange eluent (Band 3). The material remaining on the column at this point is polymeric and was discarded. Solvent removal from the first and second fractions gave a trace amount of foul-smelling, viscous liquid (discarded) and 1.29 g of a moist, orange solid, respectively. Fraction 3 gave 0.22 g of a red liquid which glpc revealed to be a 96:4 mixture of cinnamaldehyde and \( \beta \)-methylstyrene (retention times 2.1 and 0.8 min respectively), the color being due to the presence of trace polymeric material.

Fraction 4 gave 0.10 g of an orange liquid which consisted of 4 components by glpc, the major one being cinnamaldehyde. This was not analyzed further.

Fraction 5 gave 1.20 g of a pale orange solid which was reprecipitated from \( \beta \)-dioxane/hexane for easier handling. Preliminary infrared and nuclear magnetic resonance spectral data indicated this might be more of XII, however this was not confirmed.

The moist, orange solid of fraction 2 was next triturated with hexane (5 x 10 ml) separating 0.8 g of a flaky, orange solid from 0.4 g of an orange liquid. Glpc analysis showed the latter to be an 80:20 mixture
of cinnamaldehyde and β-methylstyrene. This was combined with the liquid of fraction 3 and distilled as follows. Vacuum was gradually applied to the short-path distillation apparatus with no water in the condenser, thus allowing residual solvent and β-methylstyrene to boil off at room temperature. When ebullition ceased, water was admitted to the condenser and heat applied (110°C, oil bath) causing cinnamaldehyde to distill from the polymeric materials at 41°C and 0.15 mm Hg. Yield: 0.5 g (15%).

Ultraviolet spectrum (Cyclohexane, Figure 46):

\[ \lambda_{\text{max}} 258 \text{ sh (11,400)} \text{ and } 280 \text{ nm (21,900)}. \]

Infrared spectrum (Figure 47):

684 and 745 (S,S, monosub. aromatic), 840 (W), 921 sh (W), 971 (S, trans-CH=CH-), 1004 (M), 1025 sh (W), 1070 (M), 1116 (S), 1156 (M), 1174 (M), 1198 (W), 1242 (M), 1290 (M), 1298 sh (M), 1320 (M), 1385 (W); 1444, 1485, 1568 and 1597 sh (M,W,M,S, aromatic), 1616 (S, C=C), 1655 (S, C=0), 1794 (W), 1874 (W), 1954 (W), 2222 (W); 2718 and 2785 (M,M, aldehyde C-H), 3020 (M, aromatic C-H) and 3300 cm\(^{-1}\) (W).

Nuclear magnetic resonance spectrum (CCl\(_4\), 10% w/v, Figure 48):
Figure 46. UV Spectrum of cinnamaldehyde (XIV) in Cyclohexane.
Figure 47. IR Spectrum of cinnamaldehyde (XIV).
Figure 48. NMR Spectrum of Cinnamaldehyde (XIV) in CCl₄.
09.50 (d, 1, -CHO), 7.31 (m, 5, C6H5-), 7.26 (d, 1, \( J_{ab} = 16.0 \text{ Hz}, H_a \)) and 6.54 (d of d, 1, \( J_{bc} = 7.5 \text{ Hz}, H_b \)).

Identification of 2,3-dichloro-5,6-dicyanohydroquinone dicinnamyl ether (XIII) and 2,3-dichloro-2,3-dicinnamyl -5,6-dicyanocyclohex-2-en-1,4-dione (XV). The orange solid left from the hexane trituration procedure was found to contain two components which were separated by fractional crystallization from acetone/hexane based on a solubility figure of 50 mg/ml and a solvent ratio of 1:3. Thus the material dissolved in 16 ml of acetone with slight warming to give a yellow solution. (In some cases a small amount of definite orange solid would not dissolve and was removed and combined with the orange component below.) This was heated to boiling, 50 ml of hexane added (no turbidity), and the solution cooled at 4\(^{\circ}\) for 1 hr. During this time many thin, whispy, white needles, reminiscent of glass wool, and a small number of short orange needles formed. Filtration separated the crystals from a yellow mother liquor which was momentarily set aside. Recrystallization twice more completed separation of 2,3-dichloro-5,6-dicyanohydroquinone dicinnamyl ether as pure white, intertwined needles, mp 148-149\(^{\circ}\).
Anal. Calcd for C_{26}H_{18}Cl_{12}N_{2}O_{2}: C, 67.69; H, 3.93; N, 6.07; Cl, 15.37. Found*: C, 68.03; H, 3.71; N, 6.58; Cl, 14.47.

Ultraviolet spectrum (p-Dioxane, Figure 49):

$\lambda_{\text{max}}$ 256 (42,800), 283 sh (6,620), 292 (3,820) and 325 nm (4,040).

Infrared spectrum (KBr, Figure 50):

690 and 744 (S,S, monosub. aromatic), 764 (W), 788 (W), 819 (W), 841 (M), 918 sh (M), 938 (S), 970 (S, trans-CH=CH), 1005 (S), 1025 (W), 1054 (W), 1070 (W), 1105 (W), 1153 (W), 1205 sh (W), 1225 (M), 1243 (M), 1276 (W), 1316 (M), 1355 (S), 1418 (S), 1443 (M), 1484 (W), 1536 (W), 1568 (W), 1648 (W, C=C), 2218 (W, C=N), 2918 (W, aliphatic C-H), 3002 (W, aromatic C-H) and 3390 cm^{-1} (W, O-H, KBr).

Nuclear magnetic resonance spectrum (CDCl$_3$, 5% w/v, Figure 51):

$\delta$7.32 (m, 10, C$_6$H$_5^-$), 6.67 (d, 2, $J_{ab}$ = 16.0 Hz, $H_a$), 6.43 (d of t, 2, $J_{bx}$ = 6.0 Hz, $H_b$) and 4.89 (d, 4, -CH$_2$).

The initial mother liquor was next taken to turbidity with about 50 ml of hexane and allowed to stand at room temperature for $\frac{1}{2}$ hr whereupon the second component

*Analysis by C. F. Geiger.
crystallized as very short, orange needles. Repeating
the crystallization twice gave the pure orange component
tentatively identified as 2,3-dichloro-2,3-dicyamyl-
5,6-dicyanocyclohex-2-en-1,4-dione, mp 216-217°.

Anal. Calcd for C_{26}H_{18}Cl_{2}N_{2}O_{2}: C, 67.69; H, 3.93; N,
6.07; Cl, 15.37. Found*: C, 68.77; H, 4.26; N,
4.81; Cl, 15.97.

Ultraviolet spectrum (p-Dioxane, Figure 49):
λ_{max} 257 (39,000), 285 sh (14,150) and 370 nm (1,100).

Infrared spectrum (KBr, Figure 50):
688 and 748 (S, S, monosub. aromatic), 720 (M),
773 (M), 816 (M), 850 (W), 879 (W), 902 (M),
923 (W), 971 (S, trans-CH=CH), 986 (M), 1000 (W),
1070 (W), 1102 sh (W), 1124 (S), 1157 (W),
1184 sh (S), 1200 (S), 1254 (W), 1292 (W), 1355 (W),
1428 (M); 1445 (M), 1490 (M), 1560 (S, C=C enedione)
1646 (M, C=C), 1704 (S, C=O), 2222 (W, C≡N), 2900 (M,
aliphatic C-H), 3005 (M, aromatic C-H) and 3390 cm⁻¹
(M, O-H, KBr).

Nuclear magnetic resonance spectrum (Acetone-d₆,
4.5% w/v, Figure 51):
δ7.33 (m, 10, C₆H₅−), 6.71 (d, 2, J_{ab} = 16.0 Hz,
Hₐ), 6.06 (d of t, 2, J_{bx} = 7.5 Hz, Hₗ) and 3.39
(d, 4, -CH₂).

*Analyst C. F. Geiger questioned the nitrogen value
due to lack of material.
Mass spectrum (20eV, Figure 52):

m/e 460 (M⁺) and 117 (base).

Total yield of the isomeric materials was 0.8 g (14%) of which the orange component constituted approximately 20%.

2. Comparison of the reaction rate with that of the anethole/DDQ reaction.

A 1.135 g portion of DDQ (5 mmol) was dissolved in 46 ml of benzene and mixed with a solution of 0.65 ml of β-methylstyrene (5 mmol) in 4 ml of benzene, the time being noted as 0 min. The solution was stirred magnetically as the reaction proceeded. Sequential developments were as follows: 0 min, instant intensely green (looks black) molecular complex formation on mixing; 3 min, DDHQ visible in brown-black solution; 15 min, no change; 30 min, solution deep brown; 45 min, solution red-brown; 1 hr, solution red; 2 hr, solution red, amount of tan DDHQ = 0.25 g (22%); 9 hrs, solution red; 39 hrs, solution red, trace amount of additional DDHQ formed. The reaction was thus complete in 1-2 hrs, based on a color change of black to red.

In like manner a 1.135 g portion of DDQ (5 mmol) was dissolved in 46 ml of benzene and mixed with a solution of 0.75 ml of freshly distilled anethole (5 mmol)
Figure 49. Left: UV Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone dicinnamyl ether (XIII) in p-Dioxane.

Right: UV Spectrum of 2,3-Dichloro-2,3-dicinnamyl-5,6-dicyanocyclohex-2-en-1,4-dione (XV) in p-Dioxane.
Figure 50. Top: IR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone dicinnamyl ether (XIII).
Bottom: IR Spectrum of 2,3-Dichloro-2,3-dicinnamyl-5,6-dicyanocyclohex-2-en-1,4-dione (XV).
Figure 51. Top: NMR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone dicinnamyl ether (XIII) in CDCl₃.

Bottom: NMR Spectrum of 2,3-Dichloro-2,3-dicinnamyl-5,6-dicyanocyclohex-2-en-1,4-dione (XV) in acetone-d₆.
Figure 52. 20 eV Mass Spectrum of 2,3-Dichloro-2,3-dicinnamyl-5,6-dicyanocyclohex-2-en-1,4-dione (XV).
in 4 ml of benzene, the time being noted as 0 min. The solution was swirled occasionally as the reaction proceeded. Events of the rapid and slightly exothermic reaction were: 0 min, instant intensely green (looks black) molecular complex formation on mixing; 5 sec, DDHQ visible in green solution; 20 sec, solution yellow-green; 1 min, solution yellow, amount of mint-green DDHQ = 0.57 g (50%); 2 min, no change; 15 min, no change. The reaction was, therefore, complete in 1-1\(\frac{1}{2}\) min based on a color change of black to yellow.

**H. REACTION OF \(\alpha\)-METHYLSTYRENE AND DDQ**

Twenty-five millimoles (3.23 ml) of \(\alpha\)-methylstyrene was dissolved in 20 ml of benzene and the resulting solution added to 5.67 g of DDQ (25 mmol) in 230 ml of benzene. On contact molecular complex formation produced a black solution color as in previous cases although at a somewhat slower rate. The mixture was stirred magnetically for 8 days after which 90% of the DDQ was recovered unchanged. Some DDHQ (0.3 g) was also recovered along with some \(\alpha\)-methylstyrene.

**I. REACTION OF ANETHOLE AND CHLORANIL**

A solution of 1.86 ml of anethole (12.5 mmol) in 20 ml of benzene was added to a slurry of 3.07 g of chloranil (12.5 mmol) in 150 ml of benzene. On contact molecular complex formation produced
a black solution. After 3 days there was no further visible reaction in the magnetically stirred solution. After 5 days a small amount of a reddish solid (0.15 g) was separated from polymeric material and 1.2 g (4.6 mmol) of unreacted chloranil. Further characterization of the reaction was not attempted.
Molecular complex formation is a phenomenon that has been observed throughout this work and has to some degree affected not only the spectral data obtained but also the mechanistic conclusions reached. Consequently, we preface discussion of arylpropene oxidation with an examination of this event and refer to it in subsequent pages as needed.

A. MOLECULAR COMPLEXES AND DDQ

When compounds of low ionization potential (I_D) move into proximity with those of high electron affinity (E_A) weak interaction can occur which leads to the formation of an unstable, yet discrete, species known as a molecular complex. The exact nature of the interaction is a point of current controversy, but it is known that some portion of the electron density is transferred from the highest occupied molecular orbital of the donor molecule (low I_D) to the lowest unoccupied molecular orbital of the acceptor molecule (high E_A). For the case of benzene (donor) and DDQ (acceptor), Hückel calculations suggest that the lowest unoccupied molecular orbital of DDQ is a bonding orbital (\( \alpha + 0.3848 \)), thus making complex formation energetically favorable (see Figure 53). Mulliken has suggested that complexes of this nature can exist in two energy states, \( W_n \) and \( W_e \). In the ground state (\( W_n \)), binding between the components is believed due chiefly to van der Waals interactions, including dipole
Figure 53. Relative Energies of the Huckel Molecular Orbitals for Benzene and DDQ.
orientation and induced dipole effects, with a definite though small contribution arising from the transfer of charge from the donor to the acceptor. In the excited state ($W_e$) the predominant structure is that involving complete transfer of an electron from the donor to the acceptor. Figure 54 depicts these states in correlation with potential energy curves for the formation of the benzene/DDQ molecular complex. It is evident that complex formation (a) gives rise to an absorption band characteristic of the complex, and (b) will have an effect on any chemical reaction between the donor and acceptor. Finally, the extent of the charge transfer in the ground state determines the strength of the binding, which in turn is related to the degree of complex formation (Equation 5). Values for $K_c$ have been determined in a number of cases (Table III) by kinetic as well as optical methods.$^{39,79}$

$$\text{Cl} \quad \text{Cl}$$

$$\text{K}_c = 0.47$$

B. SPECTRAL CHARACTERISTICS OF REACTANTS

1. Quinones.

DDQ. The ultraviolet spectrum of DDQ depicted two major absorptions due to $\pi \rightarrow \pi^*$ and intermolecular $\pi \rightarrow \pi$ transitions. The first results from the extended conjugation
Figure 54. Potential Energy Curves \( W \) for the Benzene/DDQ molecular complex as a function of the intercomponent distance -- illustrative only. \( W_0 \) = energy of \( \psi_0 \), wave function for no-bond state of complex; \( W_1 \) = energy of \( \psi_1 \) wave function for dative bond \( (D^+\cdots A^-) \) state of complex; \( W_n \) and \( W_e \) = energy of \( \psi_n \) and \( \psi_e \), wave functions resulting from resonance interaction of \( \psi_0 \) and \( \psi_1 \). (See R.S. Mulliken, J. Amer. Chem. Soc., 74, 811 (1952). Electron affinity value for DDQ that of Briegleb.78
of the molecule and exhibited a bathochromic shift with an increase in solvent polarity (Figure 1), a feature characteristic of such transitions. The second is a molecular complex maximum originating from intermolecular electron transfer as illustrated in Figure 54. It is worth noting that the maximum in p-dioxane is not observed unless the solvent is extremely dry. Table XI reveals that as the ionization potential of the donor increases, the molecular complex maximum suffers a hypsochromic shift (see also Figure 54). The values for benzene and acetonitrile as donor respectively indicate this trend for complexes with π-π orbital interaction; this is exemplified by the methyl- and methoxy-benzene series of Table III. The latter demonstrates the effect of steric interference with maximum orbital overlap as well. Likewise the cyclic ethers p-dioxane, tetrahydropyran, and tetrahydrofuran show the same trend for complexes with p-π orbital interaction. That there is a non-linear change between the ether series and methanol emphasizes the sensitivity of complex formation to the structural features of the donor and acceptor molecules.

The infrared spectrum of DDQ (Figure 2) has been analyzed by Baruah, Singh, and Jayaswal. Of interest were the carbonyl and double bond stretching frequencies at 1670 and 1550 cm⁻¹ respectively. The nitrile absorption was very weak in comparison with the same band in the hydroquinone.
### TABLE XI

**EFFECT OF THE IONIZATION POTENTIAL OF THE DONOR MOLECULE ON THE MOLECULAR COMPLEX MAXIMA WITH DDQ**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$I^0$ (eV)</th>
<th>Population Interaction</th>
<th>$\lambda_{CT}$ (eV)</th>
<th>$\lambda_{CT}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_6$</td>
<td>9.24</td>
<td>$\pi - \pi$</td>
<td>3.05</td>
<td>407 (2,060)</td>
</tr>
<tr>
<td>CH$_3$CN</td>
<td>12.22</td>
<td>$\pi - \pi$</td>
<td>3.60</td>
<td>345 (1,180)</td>
</tr>
<tr>
<td>p-C$_6$H$_8$O$_2$</td>
<td>9.13</td>
<td>$\pi - \pi$</td>
<td>3.26</td>
<td>380 (1,950)$^b$</td>
</tr>
<tr>
<td>THP</td>
<td>9.26</td>
<td>$\pi - \pi$</td>
<td>3.40</td>
<td>365 (1,740)$^b$</td>
</tr>
<tr>
<td>THF</td>
<td>9.54</td>
<td>$\pi - \pi$</td>
<td>3.50</td>
<td>355 (1,800)$^b$</td>
</tr>
<tr>
<td>MeOH</td>
<td>10.85</td>
<td>$\pi - \pi$</td>
<td>3.60</td>
<td>345 (500)</td>
</tr>
</tbody>
</table>


(b) Reference 41.

The mass spectrum of DDQ (Figure 3) displayed peaks at m/e 226, 228 with an unexpected isotopic ratio, indicating rapid reduction of the quinone to the hydroquinone on electron bombardment. Approximately 25% of DDHQ was present as determined from the M+2 peak, the relative abundance of which was 90.4% instead of the expected 65.3%. The M+4 peak also indicated about the same amount, for of the 28.6% abundance observed, 10.6% was expected from the DDQ molecule, leaving 18% arising
from DDHQ. The latter requires a molecular ion at m/e 228 of 27.5%. Further, the ion of 200 mass units only gave the correct isotopic peak at m/e 202 when 25% of the abundance was deleted. Finally, a metastable ion at m/e 175.2 fits only the fragmentation of DDHQ via loss of CO. Fragmentation of DDQ also occurred with loss of CO, leaving an ion of m/e 198 which fragmented further by loss of dicyanoacetylene and Cl· to the base ion at m/e 87 (Scheme IV).

TCQ. The ultraviolet spectrum of chloranil (Figure 4) was similar to that of DDQ in that absorptions resulting from extended conjugation and complex formation appeared. It was dissimilar in that (a) the molecular complex maximum did appear in p-dioxane (0.03% water present), although weakly, reflecting the lower reactivity of this quinone with water, and (b) the energy of the maximum was greater than that for DDQ, a result expected because of the lower $E_A$ of chloranil vs DDQ (1.4 vs 1.9eV).\textsuperscript{78} The interaction in this complex is, therefore, of a weaker nature than that in the benzene/DDQ complex.

The bands of interest in the infrared spectrum (Figure 2), 1560 (C=C) and 1672 cm\textsuperscript{-1} (C=O), were of slightly greater energy than the corresponding bands for DDQ perhaps reflecting the lesser degree of conjugation within the chloranil molecule.
SCHEME IV

\[
\begin{align*}
\text{Cl}_2\text{C} = \text{C} = \text{Cl} & \quad m/e = 170 \\
\text{Cl}_2\text{C} = \text{C} = \text{Cl} & \quad m/e = 146.1 \\
\text{Cl}_2\text{C} = \text{C} = \text{Cl} & \quad m/e = 198 \\
\text{Cl}_2\text{C} = \text{C} = \text{O}^+ & \\
\text{Cl}_2\text{C} = \text{C} = \text{Cl} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Cl}_2\text{C} = \text{C} = \text{O}^+ & \quad m/e = 94 \\
\text{Cl}_2\text{C} = \text{C} = \text{C} = \text{N} & \quad m/e = 87 \\
\text{Cl}_2\text{C} = \text{C} = \text{C} = \text{O}^+ & \quad m/e = 122 \\
\end{align*}
\]
No reduction of the quinone occurred in obtaining the mass spectrum (Figure 3), a further indication of the lower electron affinity, and hence reactivity, of chloranil in comparison with DDQ.

2. Arylpropenes.

For the most part the structural features of interest in the arylpropenes will be discussed in the text in comparison with the spectral properties found for various products. In passing we should note, however, that the splitting pattern and associated coupling constants shown for the nuclear magnetic resonance spectra of estragole and 1-\(\beta\)-anisylallyl ethyl ether were deduced from calculated spectra obtained from the LAOCOON II computer program.82

C. OXIDATION OF ANETHOLE BY DDQ

1. Evidence against oxidative dimerization as the course of the reaction.

Investigation of the oxidation of anethole by DDQ began with determination of the stoichiometry of the reaction. The results are given in Table VII, reproduced below for convenience, and leave no doubt that the reaction proceeds on a 1:1 mole bases and not 2:1 as previously put forth.53 Further, the nuclear magnetic resonance spectrum of the reaction mixture obtained with benzene-\(d_6\) as solvent (Figure 55) showed that the
<table>
<thead>
<tr>
<th>Anethole (mmol)</th>
<th>DDQ (mmol)</th>
<th>Mole ratio</th>
<th>Amt. DDHQ&lt;sup&gt;a&lt;/sup&gt; formed (g)</th>
<th>Percent&lt;sup&gt;b&lt;/sup&gt; DDHQ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>1:1</td>
<td>0.281</td>
<td>49.1</td>
</tr>
<tr>
<td>5.0</td>
<td>2.5</td>
<td>2:1</td>
<td>0.283</td>
<td>49.4</td>
</tr>
<tr>
<td>10.0</td>
<td>2.5</td>
<td>4:1</td>
<td>0.286</td>
<td>50.0</td>
</tr>
<tr>
<td>1.25</td>
<td>2.5</td>
<td>1:2</td>
<td>0.145</td>
<td>25.3</td>
</tr>
</tbody>
</table>

<sup>a</sup> 2,3-Dichloro-5,6-dicyanohydroquinone.

<sup>b</sup> Based on DDQ.

*p*-methoxycinnamyl moiety was the only proton-bearing species present. Thus at the outset the proposed oxidative dimerization appeared to be in error.

2. Identification of reaction products.

2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ). The solid precipitated during the reaction was identified as 2,3-dichloro-5,6-dicyanohydroquinone from the following evidence. The mass spectrum (Figure 16) gave a molecular ion at m/e 228 just two mass units above the molecular weight of the starting quinone. An isotopic peak 66% of the molecular ion at m/e 230 verified retention of
Figure 55. NMR Spectrum of the Reaction Mixture from the Anethole/DDQ Reaction with Perdeuterobenzene as Solvent.
the 2 Cl atoms in the molecule. Infrared data (Figure 14) showed the incorporation of the two hydrogen atoms as phenolic hydroxyl functions (1448 and 3220 cm\(^{-1}\)) and confirmed the presence of the nitrile group (2250 cm\(^{-1}\)). Conjugation of the latter with the ring was evident from the intense absorption displayed in the ultraviolet spectrum (Figure 13) at 247 nm (19,200). The absorption at 395 nm is explained on page 181. The presence of a very weak, concentration-dependent, phenolic signal (Table VIII) in the NMR spectrum (Figure 15) substantiated the above conclusions. The exceptionally low-field position of this signal emphasizes the electron deficiency of the aromatic nucleus, a characteristic originating from the ring substituents. In part, the downfield position is also due to intra- and intermolecular hydrogen bonding, a factor that may also be responsible for the broadness of the signal, provided that the rate of exchange between the various hydrogen-bonded species is slow on the nuclear magnetic resonance time scale. Finally, acylation of the material with acetic anhydride gave the known diacetate of 2,3-dichloro-5,6-dicyanohydroquinone, mp 182-183\(^\circ\).

2,3-Dichloro-5,6-dicyanohydroquinone bis(1-p-anisyl-propenyl) ether (I). Complete analysis of the reaction was impeded for some time due to the marked instability of I. As prepared (0.1M benzene solution, room
temperature), I demonstrated an alarming propensity to polymerize, a problem magnified at higher concentrations and temperatures. Hence, direct isolation from the reaction mixture by solvent removal was not possible. To circumvent this difficulty, several attempts were made to derivatize I.

Hydroxylation with potassium permanganate was not possible as I was rapidly attacked, suffering decomposition with evolution of hydrogen cyanide. Epoxidation with m-chloroperbenzoic acid was inconclusive. Some m-chlorobenzoic acid was recovered, but the remaining material was polymeric in nature. Bromination was also inconclusive, for only half of the theoretical amount reacted, and workup again gave polymeric materials. Catalytic hydrogenation (Pd/C) was attempted but also led to polymeric materials of I. As this was a 2:1 mole reaction, small amounts of anethole and dihydroanethole were detected as expected. Finally, in preparation for diimide reduction of I, an unusual solvolysis reaction was discovered (Section D-3, p. 167). This led to an attempt at hydrolyzing I employing p-dioxane as cosolvent, but this in effect amounted to a dioxane/water extraction of the benzene solution of I. By repeating the extraction four times more, some species (unknown at this time and perhaps acidic in nature) was extracted from the reaction mixture, for thereafter direct isolation of crude I without
polymerization was accomplished simply by solvent removal. Crystallization of the material was affected from p-dioxane/hexane as already described. Elemental analysis data confirmed the empirical formula \( \text{C}_{14} \text{H}_{11} \text{ClNO}_x \) wherein \( x \) must equal 2 as is clear from the stoichiometry of the reaction and the following spectral data.

The nuclear magnetic resonance spectrum indicated that two changes had occurred within the anethole molecule; namely, the ABX₃ splitting pattern became ABX₂, indicating removal of one of the hydrogen atoms, and the resultant methylene group resonated at 4.87δ, suggesting attachment to an electronegative center such as oxygen (compare Figures 7, 19 and 55). That these features arose from the \( \beta \)-methoxycinnamyl moiety was confirmed by infrared data (Figure 18) which included bands associated with the \( \beta \)-anisyl moiety (1244, 1450, 1504, 1568 and 1598 cm⁻¹) and a trans-disubstituted double bond (972 cm⁻¹). Presence of the nitrile group was indicated by the band at 2222 cm⁻¹.

The unique feature of the ultraviolet spectrum (Figure 17) was the intense band at 268 nm (44,200). A systematic study by Young, et al.⁶⁰ has shown that this band is characteristic of cinnamyl derivatives and generally appears near 250 nm with an intensity of 10-20,000. As Young's studies were carried out in 95% ethanol, + 5 nm must be added to our value for the \( \beta \)-dioxane solvent effect.⁸³ Likewise + 10 nm must be
added for the methoxyl substituent effect (compare Figures 5 and 9), bringing the position of the expected band into close agreement with that found. Further, we note that the intensity of the 259 nm anethole band is 20,150, and that DDHQ absorbs at 257-265 nm with an intensity of about 6,500. The value of 44,200 found for compound I thus supports the presence of two p-methoxycinnamyl units. Other bands in the spectrum included benzenoid absorptions for the hydrocarbon portion of the molecule and an additional band for the hydroquinone moiety (Table XVII).

Compound I would not give a usable mass spectrum, apparently because of its ease of decomposition resulting from the lability of the allylic ether linkages. Nevertheless, the other evidence presented is conclusive in identifying I as 2,3-dichloro-5,6-dicyanohydroquinone bis(l-p-anisylpropenyl)ether. Scheme V summarizes the 1:1 mole reaction.

3. Independent synthesis of 2,3-dichloro-5,6-dicyano-hydroquinone bis(l-p-anisylpropenyl)ether(I).

As final proof of structure, an independent mode of synthesis was sought. An initial attempt, using a literature procedure for the preparation of arylalkyl ethers, failed. Thereafter, a successful route was found which made use of the disodium salt of DDHQ and p-methoxycinnamyl chloride (Section D-2, p. 166). The
SCHEME V

\[
\begin{align*}
\text{Anethole} & \quad \text{C}_6\text{H}_6 \quad 1 \text{ min} \\
\text{DDQ} & \\
\text{Two moles} & \\
\end{align*}
\]

\[
\begin{align*}
\text{I, mp 124}^\circ\text{(dec)} & \quad (45-55\%) \\
\text{DDHQ} & \quad (100\%)
\end{align*}
\]
yield of the ether was found to be quite sensitive to the reaction conditions as shown in Table XII. It is clear that the conditions used maximize product yield while minimizing its decomposition via polymerization. Purification of the crude material by fractional crystallization has already been described. The spectral data (Figures 17, 18 and 19) and the results of the elemental analysis were identical in every respect to those for compound I, thereby unequivocally establishing the structure of I as that given. Similar hydroquinone ethers have been reported in the literature.28,30,39

**SCHEME VI**

\[
\begin{align*}
2 \text{CH}_3\text{O} & \quad \text{CH} = \text{CH}\text{-CH}_2\text{Cl} & \quad \text{Cl} \\
\quad & \quad \text{Cl} \\
\quad & \quad \text{Na}^+ \quad \text{O} \quad \text{O}^- \quad \text{Na}^+ \\
\text{C}_6\text{H}_6/\text{P-C}_4\text{H}_8\text{O}_2/\text{H}_2\text{O} & \quad \text{CN} \\
\quad & \quad \text{CN} \\
\text{CH}_3\text{O} & \quad \text{CH} = \text{CH}\text{-CH}_2\text{Cl} & \quad \text{Cl} \\
\quad & \quad \text{Cl} \\
\quad & \quad \text{O} \quad \text{O}^- \quad \text{O}^- \quad \text{Na}^+ \\
\text{Sy} & \quad \text{Syn} & \quad \text{40%}
\end{align*}
\]
4. Mechanism of the reaction.

Initial contact between anethole and DDQ results in instantaneous formation of an intensely green molecular complex that appears black to the unaided eye. The intensity of the color far exceeds that for the benzene/DDQ complex, indicating a higher concentration of the complex according to Equation 5, and thus a stronger interaction between the complex components. This is expected because of the greater electron-donating ability of anethole relative to benzene and reflects itself in a second way, namely the energy of the charge-transfer maximum (Figure 54). While the benzene/DDQ maximum is at 407 nm, that for anisole/DDQ is at 559 nm, placing that for anethole/DDQ in the 600 nm region. (The latter could...
not be measured because of the reactivity of the components; vide supra.) Thus the potential energy curves of Figure 54 are all lowered for this complex, \( W_e \) and \( W_l \) more so than \( W_o \) and \( W_n \). Mulliken has suggested that the lowering of \( W_n \) should also lower the activation barriers for some and probably all possible chemical reactions between the donor and acceptor molecules; i.e., complex formation may often be the precursor to chemical reaction\(^73\) (see Scheme VII).

As a "blocked" olefinic system, anethole does not react via dehydrogenation but instead suffers hydride\(^28\) or hydrogen atom\(^30\) abstraction by DDQ to give the coupled product 1. Distinction between these two possibilities was made from relative rate data, electron paramagnetic resonance results, and analysis of the reactions of related arylpropenes. Thus visual observation of the time required for disappearance of the color due to the molecular complex in the reaction systems anethole/DDQ and \( p \)-methylnaphthalene/DDQ suggested a rate enhancement of at least 60 times due to the methoxyl substituent. This compares with a report in the literature that the 4-methoxy derivative must be over 100 times more reactive than the parent hydrocarbon toward hydride-ion abstraction by DDQ, based on a competitive reaction study.\(^84\) By contrast the reactivity of \( p \)-methoxy -phenol,\(^85\) -thiophenol,\(^86\) and -dibenzyether\(^87\) toward the t-butoxy,
l-cyanocyclohexyl, and bromine radicals respectively, is only a maximum of 3 times greater than the reactivity of the parent compounds toward the same radicals. This agrees with the general observation that electron-donating substituents stabilize radicals of the type $X{-C}_6H_4{-Y}^\cdot$ relative to $C_6H_5{-Y}^\cdot$ to only a small degree.\(^{88,89}\) (Stabilization of radicals by electron-withdrawing substituents roughly parallels their electron-withdrawing ability.\(^{89}\)) The result found is thus strongly indicative of an ionic reaction.

Further evidence of the ionic nature of the reaction came from an electron paramagnetic resonance investigation, deemed necessary as the semiquinone, 2,3-dichloro-5,6-dicyanosemiquinone (DDSQ), of the DDQ/DDHQ redox system (Equation 6) was almost certain to be present.\(^90\)

\[
\begin{array}{c}
\text{DDQ} \\
\begin{array}{c}
\text{C}_1 \\
\text{O} \\
\text{C}_1 \\
\text{Cl} \\
\text{Cl} \\
\end{array} \\
\begin{array}{c}
\text{CN} \\
\text{CN} \\
\text{CN} \\
\text{CN} \\
\end{array}
\end{array} + \begin{array}{c}
\text{DDHQ} \\
\begin{array}{c}
\text{C}_1 \\
\text{O} \\
\text{C}_1 \\
\text{Cl} \\
\text{Cl} \\
\end{array} \\
\begin{array}{c}
\text{CN} \\
\text{CN} \\
\text{CN} \\
\text{CN} \\
\end{array}
\end{array} \rightarrow 2 \begin{array}{c}
\text{DDSQ} \\
\begin{array}{c}
\text{C}_1 \\
\text{O} \\
\text{C}_1 \\
\text{Cl} \\
\text{Cl} \\
\end{array} \\
\begin{array}{c}
\text{CN} \\
\text{CN} \\
\text{CN} \\
\text{CN} \\
\end{array}
\end{array}
\]  

Equation 6

Solutions of both reactants were prepared and analyzed in benzene, N,N-dimethylformamide, and tetrahydrofuran; DDSQ was detected in all cases. Figure 56 shows the spectrum in tetrahydrofuran (N,N-dimethylformamide is similar) while Figure 57 depicts the spectrum in benzene.
Figure 57. EPR Spectra of 2,3-Dichloro-5,6-dicyanosemiquinone (DDSQ) in benzene and Diphenylpicrylhydrazyl (DPPH).
The single line was expected since the hyperfine splitting due to the chlorine atoms in the tetrasubstituted semiquinone was very small—a result of a smaller ratio of nuclear magnetic moment to spin for $^{35}\text{Cl}$ or $^{37}\text{Cl}$ ($\mu/\hbar = 0.547$) as compared to that for $^1\text{H}$ ($\mu/\hbar = 5.58$) and as such was not resolved but contributed only to the width of the component. The form of the semiquinone was most likely the radical-ion B and not radical A, for B is symmetrical and energetically favored as both the odd electron and electron pair are uniformly distributed throughout the electron deficient molecule.

![Chemical structures](image)

Proton transfer to trace water in benzene or directly to tetrahydrofuran and N,N-dimethylformamide would explain its formation. With benzene as solvent, DDSQ is present, but only in trace amounts.

The second tracing of Figure 57 depicts the spectrum of diphenylpicrylhydrazyl (DDPH), the spectroscopic splitting factor (g-value) standard. This spectrum, and that for the field calibration standard 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, enabled
calculation of the g value for DDSQ:

\[ g_{\text{DDSQ}} = 2.0054 \] (benzene)

\[ g_{\text{DDSQ}} = 2.0048 \] (N,N-dimethylformamide)

Values of g are known to vary with ring substituents\(^9^3\) and with solvent.\(^9^4\) Thus \( p \)-benzoquinone has \( g = 2.0047 \) in water but 2.0054 in dimethylsulfoxide,\(^9^4\) while chloranil has \( g = 2.0057 \) in alkaline ethanol.\(^9^3\)

The reaction of anethole and DDQ was analyzed using a flow system such that reaction occurred directly in the probe. The field was scanned rapidly at first and then more slowly. A display of the spectrum obtained is given in Figure 58. A weak triplet, the center line of which is superimposed on the equally weak single line spectrum of DDSQ is apparent. The weak nature of the signal plus the fact that it did not change with time or increasing concentration implied that it was not associated with the anethole/DDQ reaction per se. What then was its origin? A possible answer came from the electron paramagnetic resonance spectrum of DDHQ in tetrahydrofuran (Figure 58). First, detection of DDSQ (off-scale trace) verified that the semiquinone may form by air oxidation of DDHQ itself as well as from the DDQ/DDHQ redox system. Hydroquinones have been known to undergo facile air oxidation to semiquinones for some time.\(^9^0\) Secondly, superimposed on the DDSQ signal was a weak triplet just
Figure 58. Top: EPR Spectrum of 2,3-Dichloro-5,6-dicyanohydroquinone (DDHQ) in THF.

Bottom: EPR Spectrum of the Anethole/DDQ Reaction in Benzene scanned for 5 min from the time of mixing of reactants.
as observed for the anethole/DDQ reaction. This triplet thus appears to be associated with the semiquinone and not the arylpropene. Interaction of the radical with the solvent or trace impurities therein may account for the observed multiplicity. Consistent with this idea Venkataraman, Segal and Fraenkel have noted that after several hours the single line electron paramagnetic resonance spectrum of chloranil developed additional lines, "... presumably resulting from radicals produced by side reactions." In short, with benzene as reaction solvent, it appears that free radicals were not involved in the anethole/DDQ reaction even though DDSQ was present in the reaction system in trace amounts.

The reaction of isomeric estragole (Section E, p. 176) and the hydrocarbons trans-β-methylstyrene (Section G, p. 185) and cis-β-methylstyrene with DDQ lend further support to the heterolytic nature of the reaction. In all cases trans-cinnamyl derivatives comprised the reaction products. In concert, the evidence presented suggests that subsequent to complex formation, hydride-ion transfer from anethole to DDQ occurs forming a resonance stabilized carbonium ion, viz.:

\[ \text{Ar-CH=CH-CH}_2 + \rightarrow \text{Ar-CH-CH}=CH_2 \]

which reacts with the hydroquinone anion to form compound I (Scheme VII). Similar mechanisms for related systems are recorded in
SCHEME VII

\[
\text{CH}_3\text{O} \text{CH} = \text{CH} - \text{CH}_2 \quad + \quad \text{Cl} \quad \text{O} \quad \text{CN} \quad \text{CN} \\
\xrightarrow{k_A} \quad \text{H}^- \\
\text{CH}_3\text{O} \text{CH} = \text{CH} - \text{CH}_2 \quad + \quad \text{Cl} \quad \text{O} \quad \text{CN} \quad \text{CN} \\
\xrightarrow{\text{Ar}^+} \\
\text{CH}_3\text{O} \text{CH} = \text{CH} - \text{CH}_2 \quad - \quad \text{Cl} \quad \text{O} \quad \text{CN} \quad \text{CN} \\
\xrightarrow{Q^-} \\
\text{CH}_3\text{O} \text{CH} = \text{CH} - \text{CH}_2 \quad - \quad \text{Cl} \quad \text{O} \quad \text{CN} \quad \text{CN} \\
\xrightarrow{\text{Ar}^+} \\
\text{CH}_3\text{O} \text{CH} = \text{CH} - \text{CH}_2 \quad - \quad \text{Cl} \quad \text{O} \quad \text{CN} \quad \text{CN} \
\]
Becker's proposed free radical mechanism for the reaction of diphenylmethane and DDQ (Equation 4)\textsuperscript{30} thus may be incorrect. A fact that he appears to have overlooked in his work with DDQ is that with such a strong acceptor a polar reaction medium (he used methanol in all cases except that of Equation 4) favors homolytic reactions.\textsuperscript{96}

D. REACTIVITY OF 2,3-DICHLORO-5,6-DICYANOHYDROQUINONE BIS (1-\textit{p}-ANISYLPROPENYL)ETHER

1. Oxidation by DDQ.

As the alkyl groups of compound I are arylpropenyl units bearing allylic hydrogen atoms, they are subject to further reaction with DDQ. When in fact anethole is reacted with two moles of DDQ or I is reacted with one mole of DDQ, reaction does occur, giving as products \textit{p}-methoxycinnamaldehyde and DDHQ. Identification of the hydroquinone was based on a molecular formula of \( \text{C}_8\text{H}_2\text{N}_2\text{Cl}_2\text{O}_2 \) obtained from elemental analysis and mass spectral data, derivatization to the known diacetate, and comparison of other spectral data (Figures 24 and 28) with that for authentic material. The identification of \textit{p}-methoxycinnamaldehyde and an explanation for its formation are included in the discussion of the estragole reaction (Section E, p. 176) as this is where aldehyde formation was first encountered.
2. Cleavage with hydrochloric acid.

During the early stages of structure elucidation for compound 1 it was found that the ether underwent cleavage to \( p \)-methoxycinnamyl chloride and DDHQ on reaction with hydrochloric acid (Scheme VIII). The chloride proved to be unstable, but handleable if used immediately (Section C-3, p. 151). Identification was based on physical as well as spectral data. Thus elemental analysis gave the empirical formula \( C_{10}H_{11}ClO \), which was also the molecular formula by mass spectral data (Figure 26). The base peak at m/e 147 reflects the stability of the \( p \)-methoxycinnamyl carbonium ion and hence, lability of the C-Cl bond. Other spectral data (Figures 20, 21, and 22) were also characteristic of the \( p \)-methoxycinnamyl moiety, \( \text{viz.} \):

\[
\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2-\text{X}, \quad \text{X being the electronegative chlorine atom.}
\]

The ultraviolet spectrum contained an unusual amount of fine structure and the nuclear magnetic resonance spectrum a hidden signal (lower half of \( H_a \) doublet), factors not observed in other \( p \)-methoxycinnamyl derivatives studied in this work. The chloride underwent hydrogenolysis during hydrogenation to give the known dihydroanethole (Figures 24, 25 and 26), and solvolyzed to the expected \( p \)-methoxycinnamyl ethyl ether (compare Figures 27 and 30) on treatment with
ethanol and pyridine (Scheme VIII). These facts supported the structure obtained from spectral data in every way.

**SCHEME VIII**

![Chemical structure diagram](image)
3. Solvolysis.

In spite of numerous, well-documented examples of allylic rearrangement, perusal of the literature reveals a paucity of cases in which the migrating bond moves out of conjugation with an aromatic nucleus.

\[
\text{Ar-CH=CH-CH}_2\text{X} \xrightarrow{\text{HY}} \text{Ar-CH=CH}_2 \text{X(Y)} \\
\text{Sn1' or Sn2'}
\]

Transformations of this type yield so-called "abnormal" products by either Sn1' or Sn2' mechanisms. Intuitively one would not expect such a migration to occur, and the fact that the equilibrium between 1-phenylallyl and cinnamyl compounds lies almost entirely in the direction of the latter isomer supports this view. Yet, a few examples are known. We have observed a further example of this unusual rearrangement that leads to almost exclusive formation of thermodynamically unfavored allylic ethers (abnormal products) by what is apparently an Sn2' process.

Treatment of the benzene solution of compound I with absolute ethanol at reflux for ½ hr produced the theoretical quantity of DDHQ and gave 68% of unknown 1-p-anisyl-allyl ethyl ether (II, abnormal product) and 4% of p-methoxycinnamyl ethyl ether (III, normal product).
The almost exclusive formation of II was unexpected but confirmed from spectral data. The ultraviolet spectrum (Figure 29) revealed the absence of an intense band near 268 nm and in fact was very similar to the ultraviolet spectrum of estragole rather than anethole (compare with Figure 5), implying that the double bond in ether I had moved out of conjugation with the ring on conversion to ether II. The infrared spectrum (Figure 30) confirmed this interpretation by showing that the trans-disubstituted alkene absorption at 972 cm\(^{-1}\) had been replaced by vinylic absorptions at 927 and 995 cm\(^{-1}\) again similar to estragole but not anethole (compare with Figure 6). Likewise, the nuclear magnetic resonance spectrum of II (Figure 31) paralleled that of estragole and not anethole, although there were some interesting differences. The ABX splitting pattern for protons A, B, and C in compound II was simplified relative to that for estragole as there was one less proton available for coupling; as a result the splitting was completely resolved. As required, the benzylic proton of II absorbed downfield from the benzylic protons in estragole. Finally,
the asymmetric center in the molecule induced magnetic nonequivalence into the methylene protons of the ethoxy group, resulting in a sixteen line multiplet resolved as four overlapping quartets. The spectral data for compound III (Figures 29, 30, 32 and 33), contrasted with that of ether II and compared with that of anethole, ether I, and p-methoxycinnamyl chloride, was sufficient to firmly establish the structure as p-methoxycinnamyl ethyl ether.

Ether II was also found to isomerize completely to ether III on treatment with perchloric acid, thus confirming that the major product was in fact the least stable as well. The possibility existed, therefore,

\[
\begin{align*}
\text{CH}_30\text{CH-CH=CH}_2 & \xrightarrow{\text{HClO}_4, \text{EtOH}, \text{reflux 1 hr}} \text{CH}_30\text{CH=CH-CH}_2
\end{align*}
\]

that the reaction might be totally abnormal with the small amount of III observed being formed by isomerization of II. However, this proved not to be the case as II was found to be stable to the reaction conditions employed in its formation even though the secondary reaction product was an acidic hydroquinone (Equation 10). In like manner the normal product III underwent no change under the same conditions.
It was further observed that substituting methanol, \( i \)-propanol, or \( t \)-butanol for ethanol gave the unknown methyl (IV, V), \( i \)-propyl (VI, VII) and \( t \)-butyl (VIII, IX) ethers shown below, although in differing yields (Table XIII).

\[
\begin{align*}
\text{IV} & : \text{CH}_3\text{O} - \text{CH-\text{CH=CH}_2} - \text{CH}_3 \\
\text{V} & : \text{CH}_3\text{O} - \text{CH-\text{CH=CH}_2-\text{CH} - \text{CH}_3} \\
\text{VI} & : \text{CH}_3\text{O} - \text{CH-\text{CH=CH}_2-\text{O-C\text{CH}_3}} \\
\text{VII} & : \text{CH}_3\text{O} - \text{CH-\text{CH=CH}_2-\text{O-CH}} \\
\text{VIII} & : \text{CH}_3\text{O} - \text{CH-\text{CH=CH}_2-\text{O-C\text{CH}_3}} \\
\text{IX} & : \text{CH}_3\text{O} - \text{CH-\text{CH=CH}_2-\text{O-C\text{CH}_3}}
\end{align*}
\]
The allyl-i-propyl ether VI exhibited methyl non-equivalence analogous to the proton nonequivalence observed in II. A trend of interest noted from the spectral data for these compounds occurred in the nuclear magnetic resonance spectra of the allyl alkyl ethers IV, II, VI, and VIII. As the alkyl group size increased in the order methyl, ethyl, i-propyl, t-butyl, the chemical shift of the benzylic proton increased the respective values being 4.45, 4.56, 4.68, and 4.96. The increasing bulkiness of the alkyl group thus tended to restrict rotation of the aromatic ring such that the benzylic proton moved increasingly into the ring plane thereby becoming less shielded.104

![Diagram](c)

The magnitude of the observed shift suggested other contributing interactions as well; a likely possibility would be solvent-solute interaction.
The preponderance of abnormal product can be explained by either an Sn1/Sn1' or Sn2/Sn2' process, with predominance of the abnormal reaction mode. A priori one would expect about equal reactivity for the α and γ positions of the cinnamyl carbonium ion in a unimolecular reaction, which would lead to an approximately 50:50 mixture of normal and abnormal products. The ethanolysis of cinnamyl chloride in the presence of silver ion (Equation 11), and the hydrolysis of the vinylogous compound 5-chloro-1-phenyl-1,3-pentadiene (Equation 12) support this idea.

\[
\text{\begin{align*}
\text{CH}=\text{CH}-\text{CH}_2\text{Cl} & \xrightarrow{\text{AgNO}_3, \text{EtOH}} 82\% \quad \text{CH}=\text{CH}-\text{CH}=	ext{CH}_2 \\
& \quad \text{CH}=\text{CH}-\text{CH}_2\text{OEt} \\
& \quad \text{CH}=\text{CH}-\text{CH}_2\text{OEt} \\
& \quad 60:40 \text{ mixture}
\end{align*}}
\]

Andrews has observed exclusive formation of abnormal product on solvolysis of cinnamal dichloride from a reaction which was shown to be first-order\textsuperscript{103} (Equation 13). However, this result was expected due to the much lower stability of the positive charge on the chlorine-bearing γ-carbon atom. Similar stabilities have also been noted in the unimolecular solvolysis of dichloropropenes.\textsuperscript{105} No such preference is expected for either of the canonical forms of the delocalized carbonium ion formed in our system, and since abnormal product formed almost exclusively, unimolecular solvolysis appears unlikely.

Alternatively a bimolecular reaction requires some feature that discriminates against the normal Sn2 process. A possibility would be hydrogen bonding between the alcohol and bis-ether as depicted in Scheme IX. Transition states of the type shown tend to create preferred reaction pathways when their formation is made possible by either
hydrogen\textsuperscript{106,107} or coordinate\textsuperscript{108} bonding. One would expect steric interference with the formation of such a transition state as the size of the alkyl unit of the alcohol increases. This was in fact the case as is clear from Table XIII. This mechanism is consistent with the known stereochemistry of the Sn2\textsuperscript{1} reaction\textsuperscript{98} and has analogy in the literature.\textsuperscript{106,107,108}

### TABLE XIII

PRODUCTS FROM ALCOHOLYSIS OF I IN BENZENE

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Reflux time(hr)</th>
<th>% DDHQ</th>
<th>Rearranged product(%)</th>
<th>Normal product(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>$\frac{1}{2}$</td>
<td>95</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>EtOH</td>
<td>$\frac{1}{2}$</td>
<td>93</td>
<td>68</td>
<td>4</td>
</tr>
<tr>
<td>i-PrOH</td>
<td>1</td>
<td>94</td>
<td>31</td>
<td>14</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>3</td>
<td>69</td>
<td>2</td>
<td>17</td>
</tr>
</tbody>
</table>
Two of the criteria of an Sn2¹ reaction have thus been met.¹⁰⁹ This, combined with the evidence presented, allows the tentative suggestion that with unhindered alcohols product formation in this reaction system is explained by a cyclic Sn2¹ mechanism that operates with almost total exclusion of the normal Sn2 reaction.

4. Attempted alkylation.

In a last attempt to observe the originally-reported oxidative dimerization of anethole (page 20) compound I was treated with 1 mole of anethole at elevated temperature (40⁰), and in the presence of acid (HClO₄). In the latter case it was reasoned that dimerization might be affected by assisting cleavage of the allylic ether linkages. The reaction of I with hydrochloric acid already described supported this. By replacing the hydrochloric acid with perchloric acid it was hoped that the anethole present would act as the displacing nucleophile. It did not. The only change noted was polymerization of I at high acid concentration. A different approach that may lead to new dimers of anethole has recently been reported in the literature.¹¹⁰
E. OXIDATION OF ESTRAGOLE BY DDQ

The reaction of DDQ and estragole proceeded about 30 times slower than the anethole/DDQ reaction and gave somewhat different results.

1. Identification of reaction products.

2,3-Dichloro-5,6-dicyanohydroquinone. The purple solid which precipitated during the reaction was purified and characterized as DDHQ by comparison with authentic material. In all cases the amount formed was 70-75%, signaling a reaction differing from that for anethole.

2,3-Dichloro-5,6-dicyanohydroquinone mono(1-p-anisylpropenyl) ether (X). As crystallization of the crude ether was unsuccessful, resort was made to successive re-precipitations as a means of purification. From the nuclear magnetic resonance and infrared spectra (Figures 44 and 45), initial indications were that X was identical to I. However, closer analysis of the infrared data revealed the presence of a strong hydroxyl signal at 3195 cm\(^{-1}\) not attributable to DDHQ. (The major impurity in X was DDHQ.) Further, the intensity of the characteristic ultraviolet maximum at 267 nm was roughly half that for the same band in compound I (Figure 43, see also Section G, p. 185). That these data described the mono(1-p-anisylpropenyl) ether of DDHQ was verified by elemental analysis data. Similar to compound I,
compound X solvolyzed with ethanol to an 11:1 mixture of II and III.

*p*-Methoxycinnamaldehyde (XI). A third product isolated from the reaction was the known compound *p*-methoxy-cinnamaldehyde. Identification was straightforward from melting point and spectral data (Figures 20, 21, 22). A summary of the complete reaction is given in Scheme X.

**SCHEME X**

\[
\begin{align*}
\text{Estragole} & \quad \text{C}_6\text{H}_6 \\
\text{1 hr} & \\
\text{X} & \quad 21\%, \text{ mp } = 100^\circ\text{C (dec)}
\end{align*}
\]

\[
\begin{align*}
\text{XI} & \\
\end{align*}
\]
2. Implications of aldehyde formation.

(a) Detection of unreacted estragole was unexpected. As is clear from Table XIV, its presence was not accounted for by incomplete reaction but by consumption of 5-7 mmols of DDQ by some side reaction. The constancy of the aldehyde yield (5-7 mmols), and the fact that X was the only other source of allylic protons in the system, suggested that p-methoxycinnamaldehyde might be formed by further reaction of X with DDQ, hence the reason for unreacted estragole. The only effect of increased reaction time was decomposition of X via expulsion of DDHQ.

### TABLE XIV

DATA COLLECTED FOR THE 1:1 MOLE ESTRAGOLE/DDQ REACTION

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction time (hr)</th>
<th>Amt. DDHQ (g)</th>
<th>Amt. X (g)</th>
<th>Unreacted estragole (g)</th>
<th>Amt. XI (g)</th>
<th>%a</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-5</td>
<td>½</td>
<td>3.42</td>
<td>2.4</td>
<td>1.0</td>
<td>0.7</td>
<td>17</td>
</tr>
<tr>
<td>E-1</td>
<td>1</td>
<td>4.15</td>
<td>2.0</td>
<td>0.8</td>
<td>0.4b</td>
<td>10</td>
</tr>
<tr>
<td>E-2</td>
<td>2</td>
<td>4.62</td>
<td>1.6</td>
<td>0.8</td>
<td>0.7</td>
<td>17</td>
</tr>
<tr>
<td>E-3</td>
<td>3</td>
<td>4.87</td>
<td>1.3</td>
<td>1.0</td>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>E-4</td>
<td>11½</td>
<td>5.00</td>
<td>0.9</td>
<td>0.9</td>
<td>0.6</td>
<td>15</td>
</tr>
</tbody>
</table>

*a Based on direct oxidation of estragole to p-methoxycinnamaldehyde.

b Separated by distillation instead of column chromatography.
(b) To test whether $X$ was in fact reacting with DDQ, 1:2 mole reactions were run in which complete reaction with estragole and all of $X$ was possible. This action resulted in an increase in aldehyde yield to 50% and total elimination of $X$ as an isolable reaction product, facts confirming the above supposition (Table XV). The tabular data also revealed that: (1) oxygen from the air had no effect on the yield of XI—thus a nitrogen atmosphere is not necessary as has been assumed in the past,4 (2) drop-wise addition of reactants in either order decreased the yield of aldehyde, the reason for which is not known at this time, and (3) the polymerization rate of $X$ was sufficiently large to prevent complete reaction.

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction time(hr)</th>
<th>$N_2$ Atm.</th>
<th>Initial DDHQ(g)</th>
<th>Total DDHQ(g)</th>
<th>Method of Addition</th>
<th>Amt. XI(g)</th>
<th>XI %</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-11</td>
<td>1</td>
<td>No</td>
<td>3.52</td>
<td>5.5</td>
<td>direct</td>
<td>1.0</td>
<td>50</td>
</tr>
<tr>
<td>E-6</td>
<td>2</td>
<td>No</td>
<td>4.83</td>
<td>5.4</td>
<td>&quot;</td>
<td>1.0</td>
<td>50</td>
</tr>
<tr>
<td>E-7</td>
<td>2</td>
<td>No</td>
<td>4.89</td>
<td>5.4</td>
<td>&quot;</td>
<td>1.0</td>
<td>50</td>
</tr>
<tr>
<td>E-8</td>
<td>3</td>
<td>Yes</td>
<td>a</td>
<td>b</td>
<td>0.4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>E-9</td>
<td>4</td>
<td>Yes</td>
<td>a</td>
<td>c</td>
<td>0.5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>E-10</td>
<td>14</td>
<td>Yes</td>
<td>5.51</td>
<td>5.6</td>
<td>direct</td>
<td>1.0</td>
<td>50</td>
</tr>
</tbody>
</table>

TABLE XV
EFFECT OF REACTION CONDITIONS ON THE 1:2 MOLE ESTRAGOLE/DDQ REACTION
As a result the excess quinone remaining in solution formed a molecular complex with the aldehyde thus accounting for the persistent dark color of the reaction mixture.

(c) The effect of different solvents on the reaction was also investigated, wherein benzene was replaced by p-dioxane and by methylene chloride. In both cases aldehyde yield remained unchanged but the reaction rate decreased, suggesting involvement of ionic species solvated to a higher degree than was possible with benzene as solvent.

(d) The fact that the yield of XI was just half of that expected in all cases seemed somewhat fortuitous. It was first reasoned, therefore, that the strength of the p-methoxycinnamaldehyde/DDQ molecular complex might be sufficient to prevent half of the quinone from reacting with X. At best this was a remote possibility and in fact proved not to be the case, although the yield of XI did increase slightly (Table XVI). Secondly, the source of the aldehyde oxygen had to be either the quinone itself or water present in the solvent or scavenged during workup. The slight increase in yield of XI was, therefore, significant in light of the fact that the amount of solvent used increased by 50 ml. This suggested the increase in yield might be due to water in the solvent. Andrews has reported an observation of this kind from his study on
TABLE XVI
DATA COLLECTED FOR THE 1:3 MOLE ESTRAGOLE/DDQ REACTION

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction time(hr)</th>
<th>Initial DDHQ(g)</th>
<th>% DDHQ</th>
<th>Amount XI(g)</th>
<th>% XI</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-13</td>
<td>1</td>
<td>4.47</td>
<td>52</td>
<td>1.2</td>
<td>60</td>
</tr>
<tr>
<td>E-14</td>
<td>2</td>
<td>4.86</td>
<td>57</td>
<td>1.2</td>
<td>60</td>
</tr>
</tbody>
</table>

cinnamal dichloride solvolysis.\(^{103}\) (A crude calculation based on an increase in yield of XI of 10%/50 ml of solvent showed that the required amount of water in the solvent need be only 0.02%, the exact amount indicated present in Reagent benzene by the manufacturer, Matheson Coleman & Bell.)

(e) Verification of the above hypothesis came from observations on the 1:2 mole anethole/DDQ reaction, and the effect of water on this reaction. The reaction gave results analogous to the estragole/DDQ system; conducting of the reaction in the presence of water (heterogeneous) increased the yield of XI to 80-85%. Final confirmation of water in the solvent as the source of the aldehyde oxygen came from repetition of the heterogeneous reaction in the presence of water ca. 20% enriched in \(^{18}O\). The yield of \(\rho\)-methoxycinnamaldehyde in this particular case was 85%, of which 18.8% was labeled at the aldehyde carbonyl as determined by mass spectrometry.
(Figure 23, ions at m/e 164, 149 and 133). Thus, the yield of XI is also a sensitive measure of the amount of water present in the reaction solvent.

3. Mechanism of the reaction.

The parallel between the reactions of anethole and estragole with DDQ is evident. Based on the data presented and by analogy with the previous case, the mechanism for the reaction has been formulated as presented in Scheme XI. Acetal hydrolysis is well known and was suggested as the route to formation of XI while this work was in progress.\(^8^4\) Other methods of oxidizing arylpropenes to aldehydes are known but give poorer yields.\(^1^1^1,^1^1^2\)

An explanation as to why XI did not form in the 1:1 mole anethole/DDQ reaction but was present in the analogous estragole/DDQ reaction is found in the rates of the respective reactions when ordered in the following manner, \(k_A > k_E > k_{ald}\). That is to say \(k_{ald}\) was sufficiently small and \(k_A\) large enough such that all of the quinone was consumed by the latter reaction thus precluding formation of XI. However, even though \(k_E > k_{ald}\) it was sufficiently less than \(k_A\) so that both reactions occurred. Intuitively one might expect \(k_E > k_A\), because of the favorable approach of the reactants for hydride abstraction in the molecular complex. A possible explanation as to why this was not the case comes from the realization that the
SCHEME XI

\[
\begin{align*}
\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2 + \text{Cl}_3\text{C}_6\text{H}_4\text{CN} & \rightarrow \text{Cl}_3\text{C}_6\text{H}_4\text{CN} \rightarrow \frac{k_E}{\text{H}^-}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}_2 + \text{OH}^- & \rightarrow \text{X} \rightarrow \frac{k_{ald}}{\text{DDQ}}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}-\text{CH}_2-\text{O} & \rightarrow \text{Cl}_3\text{C}_6\text{H}_4\text{CN} \rightarrow \frac{H_2O^{18}}{2 \text{DDHQ}}
\end{align*}
\]
interaction between estragole and DDQ is not as strong as that between anethole and DDQ. Based on the ideas already advanced concerning the effect of complex formation on chemical reactions (Section C-4, p. 154), the result found becomes reasonable.

F. POLYMERIZATION OF \( p \)-METHOXYSTYRENE BY DDQ

In an effort to determine if DDQ could act as a Lewis acid toward the olefinic linkage of arylpropenes, an investigation was made of the \( p \)-methoxystyrene/DDQ reaction. The only reaction observed was polymerization of the olefin. In light of recent literature studies, this appears to be an example of charge-transfer polymerization. It has been determined that DDQ is the best reagent known for effecting this type of polymerization (better than chloranil > tetracyanoethylene > maleic anhydride), and that compounds like N-vinylindole, N-vinylcarbazole, and \( p \)-methoxystyrene are easily polymerized. The mechanism for this process is unknown. An explanation is thus at hand for the persistent colors (excluding those due to molecular complex formation) noted at the end of all initial reactions in this work, i.e. charge-transfer polymerization occurred to a small extent in all cases producing small amounts of

\[
\text{CH}_3\text{O}-\text{CH} = \text{CH}_2 + \text{DDQ} \xrightarrow{\text{C}_6\text{H}_6} \text{Polymer} \quad (14)
\]
colored polymeric materials that in turn imparted color to the reaction mixtures.

G. OXIDATION OF β-METHYLSTYRENE BY DDQ

Further insight into the nature and scope of the reaction of DDQ with arylpropenes was sought through investigation of the quinone oxidation of β-methylstyrene. This hydrocarbon underwent hydride abstraction far more slowly than the p-methoxy analog (Section C, p. 145), with consequent oxidation of the product ethers to cinnamaldehyde, results analogous to those for the estragole-DDQ case. (See Scheme XII.) Identification of DDHQ and cinnamaldehyde (XIV) by comparison with authentic material and from spectral data (Figures 46, 47, 48) respectively was straightforward. The monocinnamyl ether XII, like its methoxy derivative, would not crystallize and was thus purified by reprecipitation. The ABX₂ pattern of the nuclear magnetic resonance spectrum (Figure 45); the monosubstituted aromatic and nitrile bands of the infrared spectrum (Figure 44); and the characteristic cinnamyl ultraviolet maximum at 254 nm (26,250), in comparison with the corresponding data for the methoxy derivative (X) was conclusive in identifying XII as 2,3-dichloro-5,6-dicyanohydroquinone monocinnamyl ether. Elemental analysis data was in total agreement with this structure. Bis-ether XIII was identified in the same fashion (Figures 49, 50, 51) by comparison with the corresponding methoxy derivative, I. Again elemental analysis data was in good agreement with the assigned
SCHEME XII

\[
\text{Ph} = \text{CH} = \text{CH} - \text{CH}_3 + \text{PhCl}_2 \text{Q} = \text{O} \xrightarrow{\text{Q}^-} \text{Ph} = \text{CH} = \text{CH} - \text{CH}_3
\]

\[
\text{Ph} = \text{CH} = \text{CH} - \text{CH}_2^- + \text{Cl}^- \text{Cl}^- \text{Q}^{-}\]

XII (25%)

\[
\text{Ph} = \text{CH} = \text{CH} - \text{CH}_2^- \text{O}^- \xrightarrow{\text{Q}^-} \text{Ph} = \text{CH} = \text{CH} - \text{CH}_2^- \text{O}^- \text{O}^{-}\]

XIII

\[
\text{Ph} = \text{CH} = \text{CH} - \text{CHO} + \text{DDHQ} + \text{XV}
\]

XIV (15%) (orange) (mp = 216-217°C)
structure. The presence of two cinnamyl units was deduced in part from the ultraviolet spectrum (*vide infra*).

**Compound XV.** The minor product from this reaction, compound XV, was unexpected as analogous compounds were not formed in the related systems studied. The bright orange solid had an unusually high melting point (216-217°C) and was the first of the metathetic compounds isolated in this study to give a usable mass spectrum (Figure 52). This spectrum together with the elemental analysis data revealed that compound XV was isomeric with ether XIII. Two prominent bands in the infrared spectrum at 1704 and 1560 cm⁻¹, corresponding to carbonyl and olefinic stretching frequencies respectively (Figure 50), bore close resemblance to the two primary bands in the infrared spectrum of DDQ (Figure 2) found at 1670 and 1550 cm⁻¹, suggesting the presence of an enone moiety but with some reduction in the degree of conjugation relative to that of the quinone, as indicated from the hypsochromic shift. Two possible structural units that emerge from this information are the dienone D and the enedione E. While the infrared bands of interest generally

\[
\text{Cl} \quad \text{O} \quad \text{CN} \\
\text{Cl} \quad \text{I} \quad \text{CN} \\
\text{Cl} \quad \text{O} \quad \text{CN} \\
\text{Cl} \quad \text{I} \quad \text{CN} \\
\text{D} \\
\text{O} \\
\text{E}
\]
occur at 1650 and 1620 cm\(^{-1}\) for dienones\(^{116,117}\), the corresponding values for enediones are closer to 1685 and 1580 cm\(^{-1}\).\(^{21,118}\) On this basis compound XV would contain the enedione chromophore.

The other major bands of the infrared spectrum suggested the presence of the trans-cinnamyl moiety, a fact confirmed by the characteristic ultraviolet maximum (Figure 49). This band and associated benzenoid absorptions effectively mask any \(\pi \rightarrow \pi^*\) transition that might be associated with the enedione chromophore.\(^{21}\) However, the long wavelength \(n \rightarrow \pi^*\) minimum at 370 nm (1,720) was not masked and does account for the color of the compound.

The nuclear magnetic resonance spectrum (Figure 51) showed the expected \(\text{ABX}_2\) splitting pattern but with significant differences from all previous \(\text{ABX}_2\) patterns discussed. In comparison with isomeric ether XIII the methylene absorption shifted upfield by 1.5 ppm, indicating that it was no longer adjacent to a deshielding, electronegative center such as oxygen but rather resided in the vicinity of deshielded carbon (compare with estragole, Figure 7). A position between the carbonyl and chloro groups in enedione E would meet these requirements. In addition, while the chemical shift of proton H\(_a\) and the coupling constant \(J_{ab}\) remained constant, \(\Delta\nu_{ab}\) increased as a result of an upfield shift of 0.37 ppm for proton H\(_b\). Apparently this was a further effect arising from the absence of an electronegative center adjacent to the methylene group.

One structural possibility that emerges from all of these data is 2,3-dichloro-2,3-dicinnamyl-5,6-dicyanocyclohex-2-en-1,4-dione (XV).
This structure requires that the methylene protons be accidentally equivalent for reconciliation with the nuclear magnetic resonance data obtained. Formation of the compound may be rationalized as 1,4 rather than 1,6 addition of the cinnamyl carbonium ion to the hydroquinone anion. This is reasonable as the cinnamyl carbonium ion is more reactive, and therefore less specific, than the p-methoxycinnamyl carbonium ion. Addition to the chloro-substituted olefinic bond of the molecule is expected, for experiment has proved that the cyano-substituted double bond is the more electron deficient. The mechanism of formation of XV is not known.

Ultraviolet spectra of new compounds. Comparison of the ultraviolet spectra for the new compounds presented thus far (Table XVII) clearly shows the utility of ultraviolet spectra for distinguishing between the mono and bis ether compounds, and suggests an origin for those bands not yet explained. The band at 325 nm appears to arise from the hydroquinone moiety and may be hidden in the spectrum of DDHQ. In agreement with this idea, compound XV gave no absorption at this wavelength. The lowest-energy absorption at 340 nm for the monoethers, 350 nm for DDHQ, but absent from the
### TABLE XVII

**ULTRAVIOLET SPECTRA OF COUPLED PRODUCTS FROM OXIDATION OF ARYLPROPENES BY DDQ IN p-DIOXANE**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Characteristic&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Benzenoid&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Hydroquinoid&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{max}$ (e)</td>
<td>$\lambda_2$ (e)</td>
<td>$\lambda_3$ (e)</td>
</tr>
<tr>
<td>Anethole&lt;sup&gt;b&lt;/sup&gt;</td>
<td>259(20,150)</td>
<td>288(2,470)</td>
<td>296(2,330)</td>
</tr>
<tr>
<td>X</td>
<td>267(24,800)</td>
<td>---</td>
<td>292sh(6,550)</td>
</tr>
<tr>
<td>I</td>
<td>268(44,200)</td>
<td>---</td>
<td>293sh(16,600)</td>
</tr>
<tr>
<td>$\beta$-Methylstyrene&lt;sup&gt;b&lt;/sup&gt;</td>
<td>251(14,260)</td>
<td>283(977)</td>
<td>293 (606)</td>
</tr>
<tr>
<td>XII</td>
<td>254(26,250)</td>
<td>284sh(4,300)</td>
<td>292(3,000)</td>
</tr>
<tr>
<td>XIII</td>
<td>256(42,800)</td>
<td>283sh(6,620)</td>
<td>292(3,820)</td>
</tr>
<tr>
<td>XV</td>
<td>257(39,000)</td>
<td>285sh(14,150)</td>
<td>---</td>
</tr>
<tr>
<td>DDHQ&lt;sup&gt;b&lt;/sup&gt;</td>
<td>257-265(≈6,500)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

<sup>a</sup> See reference 60.

<sup>b</sup> Included for comparative purposes.

<sup>c</sup> n + π* band, see page 188 of text.

<sup>d</sup> Absorptivity value only approximate due to solubility problems.
bis ether spectra, is ascribed to the corresponding phenoxide ions formed by transfer of the relatively acidic proton to the solvent or trace water therein (Equation 15). The bathochromic shift associated with the auxochromic anion is well known; similar observations on a related system have been reported.\textsuperscript{115}

\begin{equation}
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{R-O-H} \\
\text{CN} \quad \text{CN}
\end{array}
\xrightleftharpoons[p-\text{Dioxane(H}_2\text{O)}]{.5cm}
\begin{array}{c}
\text{Cl} \quad \text{Cl} \\
\text{R-O^-} \\
\text{CN} \quad \text{CN}
\end{array} + \text{H}_3\text{O}^+ (15)
\end{equation}

\[ \lambda_5 = 325 \text{ nm} \quad \lambda_6 = 340 \text{ nm} \]

H. REACTION OF $\alpha$-METHYLSTYRENE AND DDQ

$\alpha$-Methylstyrene and DDQ did not react beyond the point of molecular complex formation. As we have seen, the methoxy substituent, while greatly enhancing the rate of hydride abstraction

\begin{equation}
\begin{array}{c}
\text{C}_{6}\text{H}_5\text{C}=\text{CH}_2 \\
\text{CH}_3
\end{array} + \text{DDQ} \xrightarrow{\text{C}_{6}\text{H}_6, 8 \text{ days}} \text{N.R.} (16)
\end{equation}

in arylpropenes, was not necessary for reaction to occur. This result (Equation 16) suggests that an additional feature of the arylpropene molecule can regulate reactivity toward DDQ. The nature of this effect was disclosed from the ultraviolet spectrum (Figure 9). Note that the maximum is far less intense and is blue-shifted 7 nm relative to that for $\beta$-methylstyrene. This fact indicated that
steric interaction between the α-methyl group and the ortho hydrogens was sufficient to destroy the co-planarity of the Pi system, thereby reducing the degree of conjugation. In support of this supposition, Suzuki has calculated that while trans-β-methylstyrene is planar, the angle between the aromatic ring and the double bond in α-methylstyrene is about 33°.64 It is the attendant effect, viz. destabilization of the incipient carbonium ion, which may account for the result found.

I. REACTION OF ANETHOLE AND CHLORANIL

As verification of the unique oxidizing ability of DDQ in comparison with chloranil (the most widely used reagent for related oxidations), a reaction was run using the latter and the most reactive arylpropene (anethole) found in this work. The only similarity in reaction was molecular complex formation, for thereafter chloranil gave no reaction in 3 days. After 5 days the only change was a small degree of polymerization, perhaps of the same type as that reported earlier (Section F, p. 184).

J. CONCLUSION

As a high potential quinone (E_A = 1.9eV), DDQ rapidly enters into molecular complex formation with electron-rich species. A unique feature of these complexes is a charge-transfer band in the ultraviolet spectrum that shifts bathochromically as the ionization potential of the donor molecule decreases. This maximum may be used to determine the extent of complex formation, a factor that may
regulate any chemical reaction between the components as, for example, the oxidation of arylpropenes.

From the outset, the proposed oxidative dimerization of arylpropenes by DDQ appeared to be in error. Characterization of the reaction products as hydroquinone mono- and bis ethers, distinguishable in part from the intensity of a characteristic ultraviolet maximum, confirmed this idea and suggested hydride-ion or hydrogen atom abstraction as the mode of reaction. Relative rate and electron paramagnetic resonance data, correlated with observations on the reactions of related arylpropenes with DDQ, established the ionic nature of the reaction. These observations also suggested that the reactivity of arylpropenes toward DDQ may be controlled by (a) the extent of molecular complex formation, (b) the inductive and resonance effects of substituents, and (c) the planarity of the incipient carbonium ion. Thus the order of reactivity found for those arylpropenes studied was anethole > estragole > β-methylstyrene > α-methylstyrene. Allylbenzene, not studied in this work, would be expected to be more reactive than α-methylstyrene but less reactive than β-methylstyrene. A concurrent reaction found to be of minor importance was charge-transfer polymerization of the arylpropenes by DDQ. Chloranil gave no reaction with anethole.

As substituted arylpropenes, the hydroquinone ethers underwent further reaction with DDQ leading to acetals that hydrolyzed with extreme ease to aldehydes. Formation of the latter was dependent on
the rate of the initial hydride-ion abstraction reaction, and the amount of water present (heterogeneous or otherwise) in the system. These ethers also entered into an unusual allylic rearrangement on alcoholysis by what is believed to be a cyclic Sn2' mechanism. Finally, under conditions not completely defined in this work, the anion of DDHQ may suffer electrophilic attack by the cinnamyl carbonium ion, giving rise to enediones such as XV.
CHAPTER IV

LITERATURE CITED


