REACTION OF PHENOXAZINE AND PHENOTHIAZINE
WITH TETRACYANOQUINODIMETHANE*

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The corresponding α,α'-di(3-phenoxazinyl)-p-phenylenedimalononitriles and p-phenylenedimalononitrile are formed in the reaction of tetracyanoquinodimethane with phenoxazine and its heterocyclic analogs. The reaction scheme is discussed.

It was previously found that tetracyanoquinodimethane (TCQD) reacts readily with pyrroles and indoles to give 1,6-addition products [2]. Heterocyclic nitrogen compounds that have weaker donor properties such as pyridines and pyrazoles do not react with TCQD.

We have shown that TCQD reacts with phenoxazines and phenothiazines to give a new type of adduct, viz., the product of addition of two molecules of the donor to the TCQD (I) molecule, and p-phenylenedimalononitrile (II). In addition, a small amount of a colorless substance that turned blue under the influence of UV light, which is similar with respect to its behavior to the usual products of 1,6-addition to the quinoid system of TCQD and has structure III, was detected in the reaction mixture by thin-layer chromatography (TLC).

\[
\begin{align*}
&\text{TCQD} \quad \text{R} \quad \text{CN} \quad \text{C} \quad \text{R} \\
&\text{+TCQD} \quad \text{I} \quad \text{CN} \quad \text{C} \quad \text{CN} \quad \text{R} \\
&\text{II} \quad \text{X} = \text{O}, \text{S}; \text{R} = \text{H}, \text{CH}_3
\end{align*}
\]

We assume that the reaction takes place in two steps. An intermediate 1,6-addition product (III) is formed in the first step. The fact of the formation of a mixed 1,6-addition product (VI) in addition to I when the product (V) of 1,6 addition of N,N-dimethylaniline to TCQD is refluxed in alcohol in the presence of TCQD and phenoxazine or phenothiazine serves as evidence for this. The formation of VI is not observed when this reaction is carried out without TCQD.

TABLE I. Constants, Yields, and Results of Analysis of α-R-α'-R'-p-Phenylene-dimalononitriles (Ia-c, VIa,b)

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>R'</th>
<th>mp, °C</th>
<th>Found, %</th>
<th>Empirical formula</th>
<th>Calc., %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>Phenoxazinyl</td>
<td>Phenoxazinyl</td>
<td>296–297</td>
<td>497</td>
<td>C_{17}H_{14}N_{2}</td>
<td>76.2</td>
</tr>
<tr>
<td>Ib</td>
<td>Phenothiazinyl</td>
<td>Phenothiazinyl</td>
<td>280–281</td>
<td>542</td>
<td>C_{17}H_{14}N_{2}</td>
<td>71.9</td>
</tr>
<tr>
<td>Ic</td>
<td>N-Methylphenothiazinyl</td>
<td>N-Methylphenothiazinyl</td>
<td>200*</td>
<td>539</td>
<td>C_{17}H_{14}N_{2}</td>
<td>72.1</td>
</tr>
<tr>
<td>VIa</td>
<td>Phenoxazinyl</td>
<td>N,N-Dimethylaminophenyl</td>
<td>245–247</td>
<td>495</td>
<td>C_{22}H_{20}N_{2}</td>
<td>75.6</td>
</tr>
<tr>
<td>VIb</td>
<td>N,N-Dimethylaminophenyl</td>
<td>N,N-Dimethylaminophenyl</td>
<td>272 †</td>
<td>538</td>
<td>C_{22}H_{20}N_{2}</td>
<td>73.6</td>
</tr>
</tbody>
</table>

*From acetone.
†Form acetonitrile.

The second step in the reaction of TCQD with phenoxazines and phenothiazines is probably oxidation of addition product III by the acceptor to give radical IV, which then reacts with phenoxazine or phenothiazine to give I. Chloranil or benzoquinone can be used in place of TCQD as the oxidizing agent.

\[
\begin{align*}
\text{CH}_2\text{N} & \quad \text{CN} \quad \text{CN} \\
\text{CN} & \quad \text{H} \quad \text{X} \\
\text{V} & \quad \text{TCQD} \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{I} & \quad \text{+} \quad \text{+} \quad \text{+} \\
\text{VI} & \quad \text{+} \quad \text{+} \quad \text{+}
\end{align*}
\]

The existence of intermediate radical IV is confirmed by the isolation of coupling product VII, if TCQD or chloranil is refluxed in acetonitrile with V.

\[
\begin{align*}
\text{V} & \quad \text{+} \quad \text{O} \\
\text{R} \quad \text{R} \quad \text{R} \\
\text{VI} & \quad \text{R} \quad \text{OH} \quad \text{OH} \\
\text{R} & \quad \text{H} \quad \text{Cl}
\end{align*}
\]

To establish the structure of I we studied the reaction of TCQD with N-methylphenothiazine, which proceeds in the same way as its reaction with phenothiazine. This excludes reaction at the nitrogen atom in the phenothiazine molecule in the first step. If the para position relative to the nitrogen atom in the phenothiazine molecule is occupied, as, for example, in 3,7-dimethylphenothiazine, the reaction with TCQD stops at the step involving the formation of the molecular complex even under severe conditions (refluxing in dimethylformamide). Thus the addition of TCQD in the first step takes place in the para position relative to the nitrogen atom in the donor molecule.

To ascertain the site of Incorporation of radical IV in the phenothiazine molecule in the second step we carried out the reaction of TCQD and V with 3,7-dimethylphenothiazine. The formation of an addition product of the VI type is not observed in this case. Thus in the second step the addition of radical IV also takes place in the para position relative to the nitrogen atom in the donor molecule.

Compounds I and VI are crystalline colorless substances; their constants are presented in Table 1.