Oxidation of 3,5,3′,5′-Tetra-tert-butyl-4,4′-dihydroxybiphenyl with Atmospheric Oxygen in the Absence of Base Catalysts

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Abstract—Use of dimethylformamide as solvent and preliminary addition of 3,5,3′,5′-tetra-tert-butyl-4,4′-diphenooquinone allow oxidation of 3,5,3′,5′-tetra-tert-butyl-4,4′-dihydroxybiphenyl with atmospheric oxygen to be efficiently performed in the absence of base catalysts.

The use of oxidants capable of regeneration by oxidation of their reduced forms with atmospheric oxygen shows promise in industrial oxidations. Such oxidants can be used repeatedly without accumulation of their reduced forms, which often form the main body of production waste.

One of such oxidants is a mild dehydrogenating agent, 3,5,3′,5′-tetra-tert-butyl-4,4′-diphenooquinone I [1]. Its reduced form, 3,5,3′,5′-tetra-tert-butyl-4,4′-dihydroxybiphenyl II, can be readily oxidized with atmospheric oxygen in the presence of base catalysts [2] [scheme (1)].

![Equation](image)

Redox reactions between sterically hindered phenols and quinones with the formation of phenoxyl radicals were reported in [8–11]. Such a transformation in the system phenol II–quinone I was discussed in [12], and formation of phenoxyl radical III [scheme (2)] was presumed.

Oxidation of phenol II with atmospheric oxygen in various solvents (6 h, 90–100°C, cH 0.25 M)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>cF, M</th>
<th>Yield of quinone I, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>0</td>
<td>18</td>
</tr>
<tr>
<td>DMF</td>
<td>0.025</td>
<td>20</td>
</tr>
<tr>
<td>DMF</td>
<td>0.25</td>
<td>60</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.25</td>
<td>15</td>
</tr>
<tr>
<td>DMF–H2O, 20:1</td>
<td>0.25</td>
<td>70</td>
</tr>
<tr>
<td>DMF–H2O, 10:1</td>
<td>0.25</td>
<td>80</td>
</tr>
</tbody>
</table>

a In the initial mixture. b After subtraction of the amount of I initially added to the solution.
ESR spectrum of phenoxyl radical $\text{III}$ (323 K, $c_{\text{I}} = c_{\text{II}} = 5 \times 10^{-3}$ M).

This equilibrium can account for the effect of $\text{I}$ on oxidation of $\text{II}$. Namely, in the first stage, radicals $\text{III}$ are generated by relatively fast dehydrogenation of the substrate, whereas in the absence of $\text{I}$ radicals $\text{III}$ are generated by slow [13] oxidation of un-ionized phenol $\text{II}$ with atmospheric oxygen [scheme (3)]. This is followed by reactions (4) and (5).

$$\text{II} + \text{O}_2 \rightarrow \text{III} + \text{HO}_2^\cdot \tag{3}$$

$$\text{III} + \text{HO}_2^\cdot \rightarrow \text{I} + \text{HOOH} \quad \downarrow \quad \text{H}_2\text{O} + \frac{1}{2}\text{O}_2, \tag{4}$$

$$\text{III} + \text{O}_2 \rightarrow \text{I} + \text{HO}_2^\cdot \tag{5}$$

The fact that, for significant acceleration of the oxidation of $\text{II}$, the amount of $\text{I}$ should be comparable with that of $\text{II}$, and not catalytic, counts in favor of such a mechanism. Furthermore, we detected radicals $\text{III}$ in toluene solutions containing equimolar amounts of $\text{II}$ and $\text{I}$ by ESR spectroscopy (see figure). The multiplicity of the signal (1 : 4 : 6 : 4 : 1) and its parameters (hyperfine coupling constant 1.67 Oe, $g$-factor 2.004) coincide with the published data [14]. The low intensity of the signal, decreasing with temperature, shows that the concentration of radicals $\text{III}$ is low and is determined by the equilibrium constant of reaction (2).

Oxidation of $\text{II}$ in the presence of $\text{I}$ can be regarded as a self-conjugated process in which oxidation of $\text{II}$ with atmospheric oxygen is conjugated with its dehydrogenation under the action of $\text{I}$.

Thus, regeneration of quinone $\text{I}$ from its reduced form $\text{II}$ can be efficiently performed with atmospheric oxygen in DMF in the absence of base catalysts. Preliminary addition of quinone $\text{I}$ results in noticeable acceleration of the reaction owing to the occurrence of a self-conjugated process.

**EXPERIMENTAL**

The ESR spectra of $\text{III}$ were recorded on a Radiopan SE/X-2544 spectrometer. The solution was deaerated by threefold freezing–pumping–thawing.

**Oxidation of 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxybiphenyl $\text{II}$.** A solution of 1 g of phenol $\text{II}$ and 1 g of quinone $\text{I}$ in 10 ml of dimethylformamide was placed in a reactor equipped with an efficient reflux condenser and an adapter for air bubbling. Through the reaction mixture heated to 90–100°C, air was bubbled for 6 h at a rate of 39 l h$^{-1}$. Then the mixture was cooled to room temperature, and the precipitate of $\text{I}$ was filtered off.

Oxidation of $\text{II}$ in other solvents and without addition of $\text{I}$ was performed similarly.

**REFERENCES**

OXIDATION OF 3,5,3',5'-TETRA-tert-BUTYL-4,4'-DIHYDROXYBIPHENYL


