2,5-CYCLOHEXADIENONES, 1. A NOVEL FORMATION OF 1-(3,5-DI-t-BUTYL-2-HYDROXYPHENYL)PYRIDINIUM BROMIDE

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Abstract — The reaction of 4-bromo-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (1) with pyridine (3) afforded 1-(3,5-di-t-butyl-2-hydroxyphenyl)pyridinium bromide (2) in 20% yield, which gave easily 2,4-di-t-butyl-6-(1-pyridinyl)phenolate (12) by the treatment with strong base such as DBU. It was also found in this reaction that addition of ethylene glycol increased the yield of 2 from 20% to 45%. The reduction of 2 with sodium borohydride afforded same product, 2,4-di-t-butyl-6-(1,2,3,6-tetrahydro-1-pyridyl)phenol (13). A tentative mechanistic interpretation for the formation of 2 is also proposed.

It has been previously reported that 2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (1) reacted with alcohols,1 sodium phenolates2 and amines such as piperidine and morpholine3 to afford the corresponding 4-substituted 2,4,6-tri-t-butyl-2,5-cyclohexadien-1-ones (2), respectively.

In contrast to these reactions, the reaction of 1 with pyridine (3) in molar ratio of 1 : 2 at 110 °C (bath temperature) for 1 hr without solvent, however, afforded unexpected product, 1-(3,5-di-t-butyl-2-hydroxyphenyl)pyridinium bromide (4) [mp 300 °C (d.), colorless needles] in 20% yield together with 2,4,6-tri-t-butylphenol5-
6, 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadien-1-one\(^6\) (\(\xi\)), and 2,6-di-t-butylbenzoquinone\(^7\) (\(\eta\)), respectively. Isobutylene (\(\delta\)) was generated during the reaction as a gaseous product which was led by nitrogen stream into a mixture of toluene and small amount of aluminium chloride to give t-butyltoluens (\(\zeta\)).

\[
\begin{array}{c}
\text{\(\xi\)} + \text{toluene} \xrightarrow{1 \text{ hr}} \text{\(\zeta\)} + \text{t-butyltoluenes}
\end{array}
\]

It was also found that addition of ethylene glycol\(^8\) of molar ratio of 1 : 1 to \(\eta\) in this reaction increased the yield of \(\xi\) from 20% to 45%. However, it is not clear why such different results are obtained.

Treatment of \(\xi\) with strong base such as DBU afforded a known compound,\(^9a\) 2,4-di-t-butyl-6-(1-pyridinio)phenolate\(^9b\) (\(\lambda\)), mp 180°C (d.), dark violet needles\(^10\) in almost quantitative yield. The compound \(\zeta\) was again regenerated from \(\lambda\) by treatment with hydrobromic acid. The reduction of \(\xi\) and \(\lambda\) with sodium borohydride gave same product, 2,4-di-t-butyl-6-(1,2,3,6-tetrahydro-1-pyridyl)phenol\(^11\) (\(\mu\)), mp 71-73°C, colorless needles. The structures of all products are supported by their elemental analyses, nmr and ir spectral data.

\[
\begin{array}{c}
\text{\(\xi\)} \xrightarrow{DBU} \text{\(\lambda\)} \xrightarrow{NaBH}_4 \text{\(\mu\)}
\end{array}
\]

It was also found that 2-bromo-4,6-di-t-butylphenol (\(\nu\)) did not react with \(\eta\) under same conditions used and that 4-bromo-2,6-di-t-butylphenol (\(\lambda\)) afforded in 85% yield 3,5,3',5'-tetra-t-butyldiphenoxiquinone (\(\omega\)).\(^12\) These results clearly suggest that bromophenols such as \(\nu\) and \(\lambda\) are not intermediate for the formation of \(\zeta\).
Based on the above results, our tentative mechanistic interpretation for the production of 4 is proposed as the following scheme.

The debutylation at 2-position of an intermediate B might take place more easily than that at 4-position of an intermediate A, that is, $k_o > k_p$. Therefore, the ortho isomer 4 was selectively formed but not the para isomer 4'.

REFERENCES AND NOTES

4. IR (KBr); $v_{max} = 3400, 2680-2520, 1630, 1610$ cm$^{-1}$.
8. When excess amount of ethylene glycol was used, the corresponding alkoxy derivative was obtained.

\[ \frac{1}{2} \quad + \quad \text{HOCH}_2\text{CH}_2\text{OH} \quad \xrightarrow{\beta} \quad \text{O} \quad \text{CH}_2\text{CH}_2\text{OH} \]


9b. $^1\text{H-nmr (CDCl}_3\text{)}$: $\delta = 1.30$ (s, 9H), 1.50 (s, 9H), 6.96 (d, $\downarrow$ 3Hz, 1H), 7.38 (d, $\downarrow$ 3Hz, 1H), 8.18 (m, 1H), 9.10 (m, 2H); $^{13}\text{C-nmr (CDCl}_3\text{)}$: $\delta = 29.48$ (q), 31.61 (q), 33.81 (s), 35.82 (s), 117.20 (d), 126.09 (d), 126.27 (d), 130.41 (s), 131.21 (s), 140.95 (d), 142.47 (s), 144.73 (d), 159.34 (s).

10. The mono hydrate ($\text{C}_{19}\text{H}_{25}\text{NO}\cdot\text{H}_2\text{O}$) is orange red needles. The tetra hydrate ($\text{C}_{19}\text{H}_{25}\text{NO}\cdot\text{4H}_2\text{O}$) is orange yellow needles.

11. $^1\text{H-nmr (CDCl}_3\text{)}$: $\delta = 1.30$ (s, 9H), 1.41 (s, 9H), 2.30 (m, 2H), 2.98 (Ca, t, $\downarrow$ 6Hz, 2H), 3.36 (m, 2H), 5.78 (m, 2H), 6.28 (broad s, 1H, disappeared with D$_2$O), 7.04 (d, $\downarrow$ 3Hz, 1H), 7.10 (d, $\downarrow$ 3Hz, 1H); $^{13}\text{C-nmr (CDCl}_3\text{)}$: $\delta = 26.90$ (t), 29.48 (q), 31.67 (q), 34.50 (s), 34.89 (s), 49.80 (t), 52.24 (t), 115.88 (d), 120.46 (d), 125.04 (d), 125.72 (d), 133.91 (s), 138.73 (s), 140.98 (s), 147.99 (s).


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