

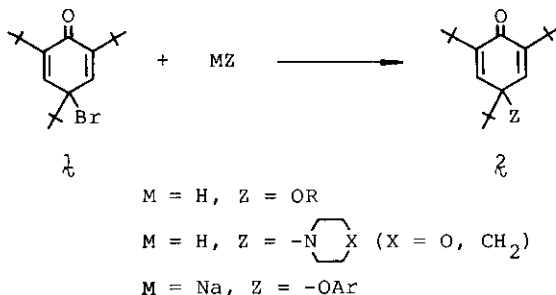
2,5-CYCLOHEXADIENONES. 1. A NOVEL FORMATION OF 1-(3,5-DI-*t*-BUTYL-2-HYDROXYPHENYL)PYRIDINIUM BROMIDE

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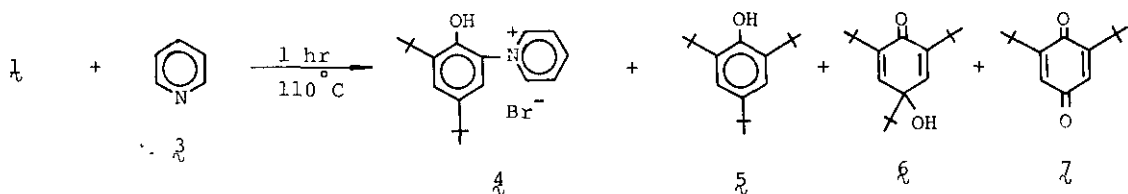
Abstract — The reaction of 4-bromo-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (**1**) with pyridine (**2**) afforded 1-(3,5-di-*t*-butyl-2-hydroxyphenyl)pyridinium bromide (**3**) in 20% yield, which gave easily 2,4-di-*t*-butyl-6-(1-pyridinio)phenolate (**4**) by the treatment with strong base such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

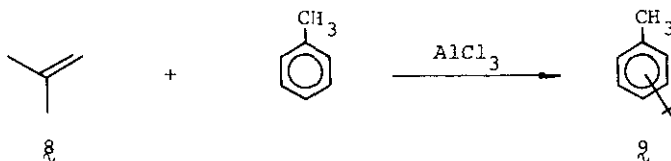


In contrast to these reactions, the reaction of **1** with pyridine (**2**) in molar ratio of 1 : 2 at 110°C (bath temperature) for 1 hr without solvent, however, afforded unexpected product, 1-(3,5-di-*t*-butyl-2-hydroxyphenyl)pyridinium bromide⁴ [**3**, mp 300°C (d.), colorless needles] in 20% yield together with 2,4,6-tri-*t*-butylphenol⁵-

(5), 2,4,6-tri-*t*-butyl-4-hydroxy-2,5-cyclohexadien-1-one⁶ (6), and 2,6-di-*t*-butylbenzoquinone⁷ (7), respectively. Isobutylene (8) was generated during the reaction

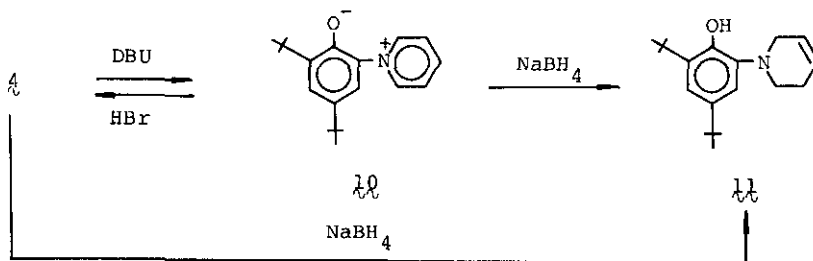


as a gaseous product which was leaded by nitrogen stream into a mixture of toluene and small amount of aluminium chloride to give *t*-butyltoluenes (9).

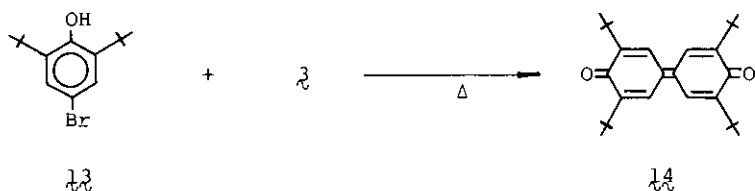
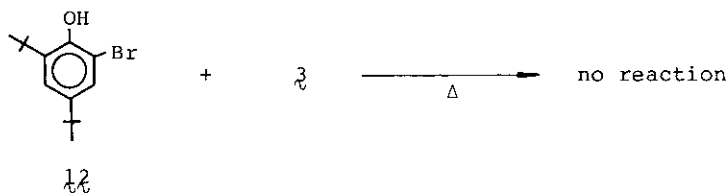


It was also found that addition of ethylene glycol⁸ of molar ratio of 1 : 1 to 1 in this reaction increased the yield of 4 from 20% to 45%. However, it is not clear why such different results are obtained.

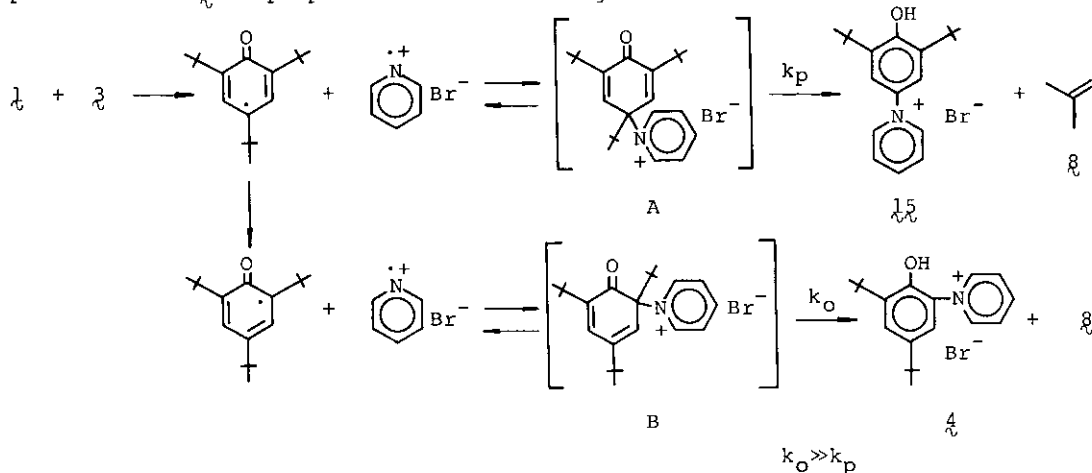
Treatment of 4 with strong base such as DBU afforded a known compound,^{9a} 2,4-di-*t*-butyl-6-(1-pyridinio)phenolate^{9b} [10, mp 180°C (d.), dark violet needles¹⁰] in almost quantitative yield. The compound 4 was again regenerated from 10 by treatment with hydrobromic acid. The reduction of 4 and 10 with sodium borohydride gave same product, 2,4-di-*t*-butyl-6-(1,2,3,6-tetrahydro-1-pyridyl)phenol¹¹ [11, mp 71-73°C, colorless needles]. The structures of all products are supported by their elemental analyses, nmr and ir spectral data.



It was also found that 2-bromo-4,6-di-*t*-butylphenol (12) did not react with 3 under same conditions used and that 4-bromo-2,6-di-*t*-butylphenol (13) afforded in 85% yield 3,5,3',5'-tetra-*t*-butyldiphenoquinone (14).¹² These results clearly suggest that bromophenols such as 12 and 13 are not intermediate for the formation of 4.



Based on the above results, our tentative mechanistic interpretation for the production of 4 is proposed as the following scheme.

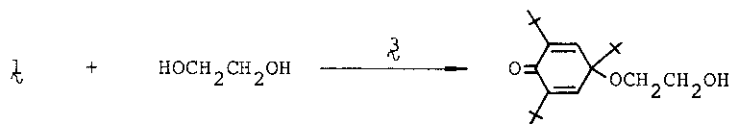


The debutylation at 2-position of an intermediate B might take place more easily than that at 4-position of an intermediate A, that is, $k_o \gg k_p$. Therefore, the ortho isomer 4 was selectively formed but not the para isomer 15.

REFERENCES AND NOTES

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2. M. Tashiro, H. Yoshiya, and T. Yamato, Synthesis, 1978, 399.
3. M. Tashiro and G. Fukata, Synthesis, in press.
4. IR (KBr); ν_{max} = 3400, 2680-2520, 1630, 1610 cm^{-1} .
5. M. Tsubota, Nippon Kagaku Zasshi, 1968, 89, 602.
6. N. Nishinaga, T. Itahara, and T. Matsuura, Bull. Chem. Soc. Japan, 1975, 48, 1683.
7. A. McKillop and B. P. Swann, Tetrahedron, 1970, 26, 4031.

8. When excess amount of ethylene glycol was used, the corresponding alkoxy derivative was obtained.



- 9a. G. Popp and N. C. Reitz, *J. Org. Chem.*, 37, 3646 (1972).
- 9b. ^1H -nmr (CDCl_3): $\delta = 1.30$ (s, 9H), 1.50 (s, 9H), 6.96 (d, $\underline{\text{J}}$ 3Hz, 1H), 7.38 (d, $\underline{\text{J}}$ 3Hz, 1H), 8.18 (m, 1H), 9.10 (m, 2H); ^{13}C -nmr (CDCl_3): $\delta = 29.48$ (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 ($\text{C}_{19}\text{H}_{25}\text{NO}\cdot 4\text{H}_2\text{O}$) is orange yellow needles.
11. ^1H -nmr (CDCl_3): $\delta = 1.30$ (s, 9H), 1.41 (s, 9H), 2.30 (m, 2H), 2.98 (Ca, t, $\underline{\text{J}}$ 6Hz, 2H), 3.36 (m, 2H), 5.78 (m, 2H), 6.28 (broad s, 1H, disappeared with D_2O), 7.04 (d, $\underline{\text{J}}$ 3Hz, 1H), 7.10 (d, $\underline{\text{J}}$ 3Hz, 1H); ^{13}C -nmr (CDCl_3): $\delta = 26.90$ (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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