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

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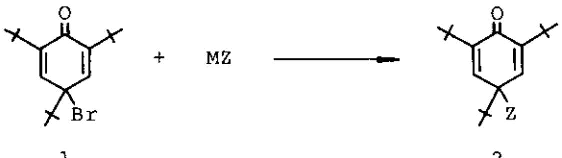
Abstract — The reaction of 4-bromo-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (**1**) with pyridine (**3**) afforded 1-(3,5-di-t-butyl-2-hydroxyphenyl)pyridinium bromide (**4**) in 20% yield, which gave easily 2,4-di-t-butyl-6-(1-pyridinio)phenolate (**10**) by the treatment with strong base such as DBU. It was also found in this reaction that addition of ethylene glycol increased the yield of **4** from 20% to 45%. The reduction of **4** and **10** with sodium borohydride afforded same product, 2,4-di-t-butyl-6-(1,2,3,6-tetrahydro-1-pyridyl)phenol (**11**). A tentative mechanistic interpretation for the formation of **4** 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 phenolates[2] and amines such as piperidine and morpholine[3] to afford the corresponding 4-substituted 2,4,6-tri-t-butyl-2,5-cyclohexadien-1-ones (**2**), respectively.

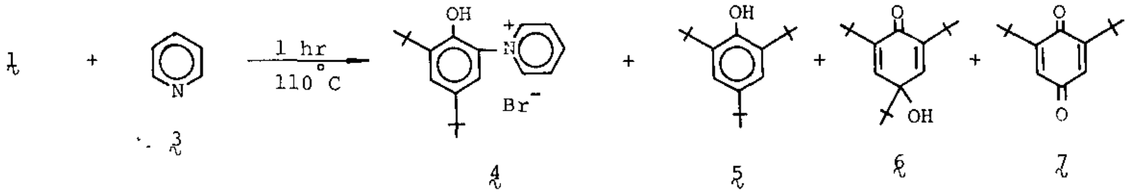


1 **2**

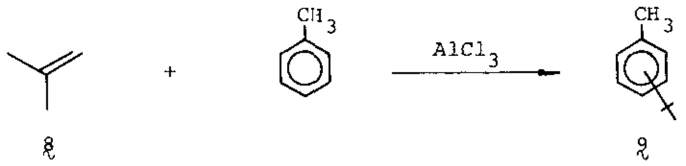
M = H, Z = OR
M = H, Z = -N X (X = O, CH$_2$)
M = Na, Z = -OAr

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] [**4**, mp 300°C (d.), colorless needles] in 20% yield together with 2,4,6-tri-t-butylphenol[5]-

(5), 2,4,6-tri-t-butyl-4-hydroxy-2,5-cyclohexadien-1-one[6] (6), and 2,6-di-t-butylbenzoquinone[7] (7), respectively. Isobutylene (8) was generated during the reaction

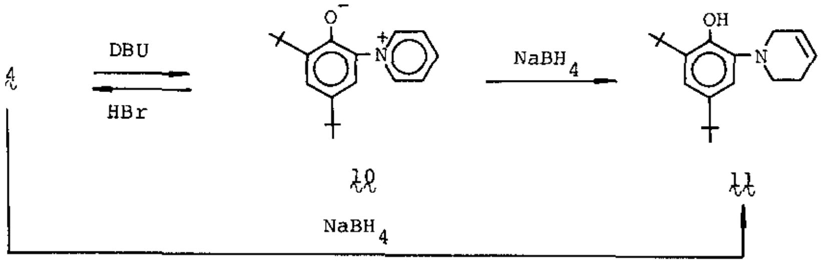


as a gaseous product which was leaded by nitrogen stream into a mixture of toluene and small amount of aluminium chloride to give t-butyltoluenes (9).

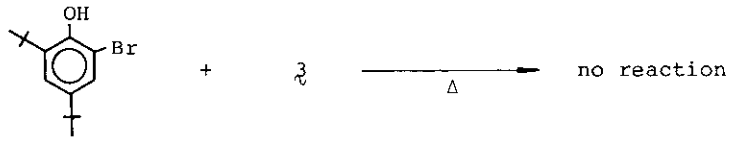


It was also found that addition of ethylene glycol[8] of molar ratio of 1 : 1 to 1 in this reaction increased the yield of 4 from 20% to 45%. However, it is not clear why such different results are obtained.

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 needles[10]] 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)phenol[11] [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.



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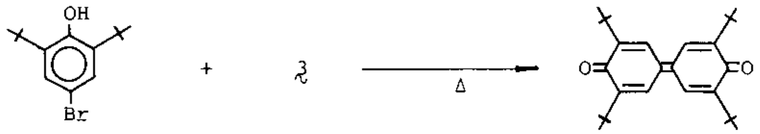

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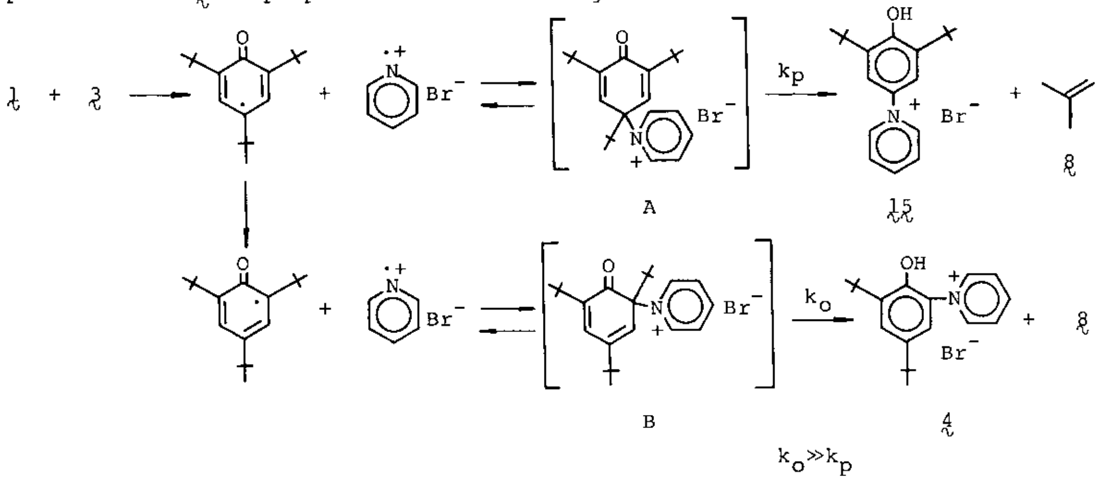
Based on the above results, our tentative mechanistic interpretation for the production of 4 is proposed as the following scheme.



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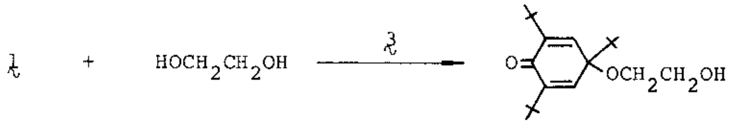
8. When excess amount of ethylene glycol was used, the corresponding alkoxy derivative was obtained.



9a. G. Popp and N. C. Reitz, J. Org. Chem., 37, 3646 (1972).

9b. ^{1}H-nmr ($CDCl_3$): δ = 1.30 (s, 9H), 1.50 (s, 9H), 6.96 (d, *J* 3Hz, 1H), 7.38 (d, *J* 3Hz, 1H), 8.18 (m, 1H), 9.10 (m, 2H); ^{13}C-nmr ($CDCl_3$): δ = 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 ($C_{19}H_{25}NO\cdot H_2O$) is orange red needles. The tetra hydrate ($C_{19}H_{25}NO\cdot 4H_2$) is orange yellow needles.

11. ^{1}H-nmr ($CDCl_3$): δ = 1.30 (s, 9H), 1.41 (s, 9H), 2.30 (m, 2H), 2.98 (Ca, t, *J* 6Hz, 2H), 3.36 (m, 2H), 5.78 (m, 2H), 6.28 (broad s, 1H, disappeared with D_2O), 7.04 (d, *J* 3Hz, 1H), 7.10 (d, *J* 3Hz, 1H); ^{13}C-nmr ($CDCl_3$): δ = 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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