

REACTIONS OF 4-HALO-2,4,6-TRI-*t*-BUTYL-2,5-CYCLOHEXADIEN-
1-ONES WITH AMINES

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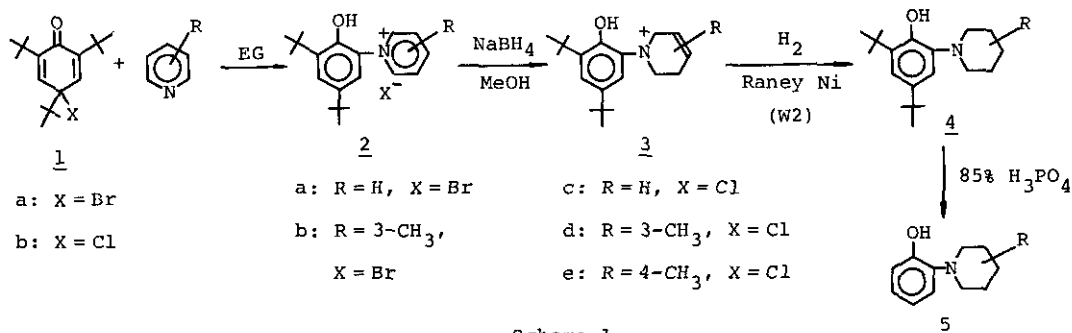
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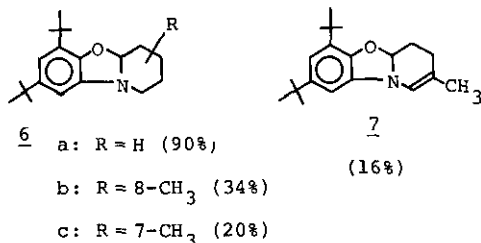
Reaction of 4-bromo-(1a) and 4-chloro-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (1b) with N-contained heteroaromatic compounds such as pyridines, imidazoles, benzimidazoles, pyrazoles, pyrroles and pyrimidine was investigated.

Reaction of 1a and 1b with pyridines in the presence of ethylene glycol (EG) at 110°C (bath temperature) afforded 1-(3,5-di-*t*-butyl-2-hydroxyphenyl)pyridinium halides (2) in moderate yields, respectively. Reduction of 2 with NaBH₄ in methanol gave 2,4-di-*t*-butyl-6-(1,2,3,6-tetrahydro-1-pyridyl)phenols (3) which were easily reduced to 2,4-di-*t*-butyl-6-piperidinophenols (4) by Raney Ni (W2) catalyzed hydrogenation. De-*t*-butylation of 4 in refluxing 85% H₃PO₄ afforded corresponding 2-piperidinophenols (5) in good yields, respectively (Scheme 1).



Scheme 1

On the preparation of 4 from 2 in one step, the reduction of 4 was carried out with Raney Ni-Al alloy in an alkaline solution. The expected compounds were not formed however, but the reductive cyclization occurred and yielded the novel



products 6 and 7 in shown below.

The reaction of 1 with imidazoles, benzimidazoles and pyrazoles also gave the expected products, respectively. The reaction of 1 with pyrroles and pyrimidine, however, gave no any reaction products.