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

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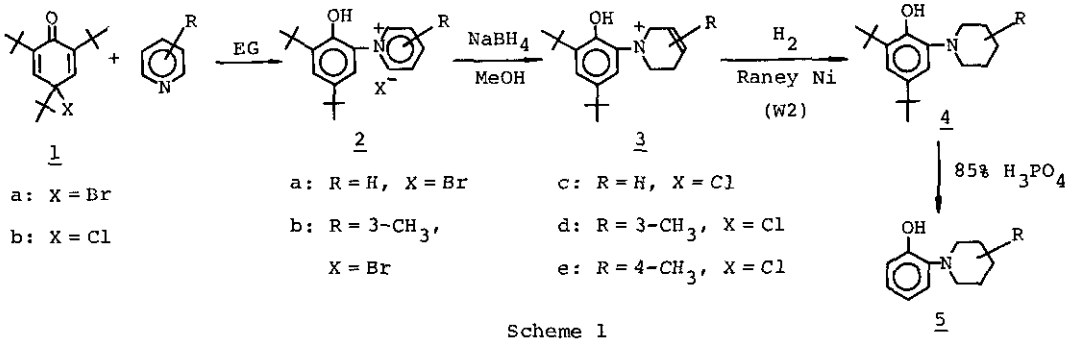
Reaction of 4-bromo-(1a) and 4-chloro-2,4,6-tri-t-butyl-2,5-cyclohexadien-1-one (1b) with N-contained heteroaromatic compounds such as pyridines, imidazoles, benzimidazoles, pyrazoles, pyrroles and pyrimidine was investigated.

Reaction of 1a and 1b with pyridines in the presence of ethylene glycohol (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 $NaBH_4$ 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% H_3PO_4 afforded corresponding 2-piperidinophenols (5) in good yields, respectively (Scheme 1).



1

a: X = Br

b: X = Cl

2

a: R = H, X = Br

b: R = 3-CH_3, X = Br

3

c: R = H, X = Cl

d: R = 3-CH_3, X = Cl

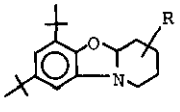
e: R = 4-CH_3, X = Cl

4

5

Scheme 1

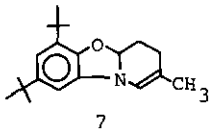
On the preparation of 4 from 2 in one step, the reduction of 4 was carried out with Raney Ni-Al alloy in an alkaline solution. The expected compounds were not formed however, but the reductive cyclization occurred and yielded the novel products 6 and 7 in shown below.



6 a: R = H (90%)

b: R = 8-CH_3 (34%)

c: R = 7-CH_3 (20%)



7 (16%)

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.