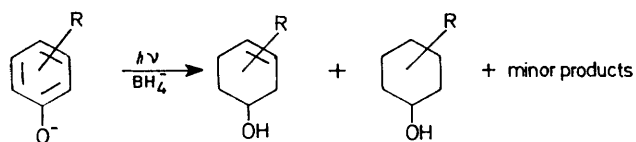


Deuterium-labelling Study of the Photoreduction of Phenols by Sodium Borohydride

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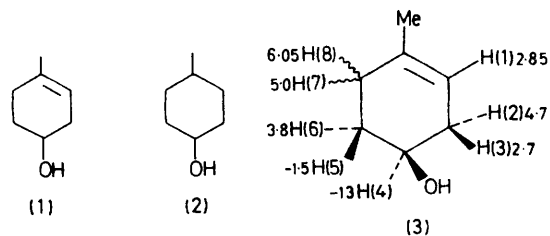
Summary Deuterium-labelling experiments have been performed in order to elucidate the mechanism of photoreduction of phenols by sodium borohydride; the results suggest the interaction of phenoxyl radicals successively with borohydride (*via* a cyclic mechanism) and with solvated electrons.

WITKOP and WATERS¹ demonstrated that the phenolic ring of 3,17 β -estradiol could be photoreduced by borohydride to the corresponding cyclohexenol and cyclohexanol. Stimulated by this report and in continuation of our studies of photochemical reduction² with borohydride,³ we have examined the photoreduction of simple phenols.



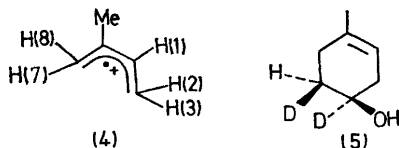
We find that phenol and its singly and doubly methylated derivatives when irradiated with BH_4^- in alkaline aqueous solution undergo reduction (in poor yield) according to the reactions in Scheme 1. *p*-Cresol was selected for detailed

study. It was irradiated with NaOH and NaBH_4 (molar ratio 1:2:2) in H_2O solution giving the products (1) and (2). For deuterium-labelling studies it was essential to be able to identify the n.m.r. signals due to each ring proton in the products. For (1), this was accomplished through the use of the paramagnetic shift reagent tris-heptafluorodimethyloctanedionateuropium(III) in CDCl_3 solution, with a molar ratio of shift reagent to cyclohexenol of 0.3:1. Extensive decoupling experiments, combined with the results of other workers⁴ permitted the τ values of the shifted n.m.r. signals of (1) to be assigned as depicted in (3).



When *p*-cresol was irradiated in $\text{NaOH-NaBD}_4\text{-H}_2\text{O}$ the n.m.r. spectrum of the 4-methylcyclohexenol obtained indicated the incorporation of $80 \pm 20\%$ D at H(5) and $> 80\%$ D at H(4), (5), with no detectable deuterium else-

where. This general distribution was confirmed by mass spectrometry, for the retro-Diels-Alder fragment (4) contained no measurable deuterium. Conversely, the methyl-

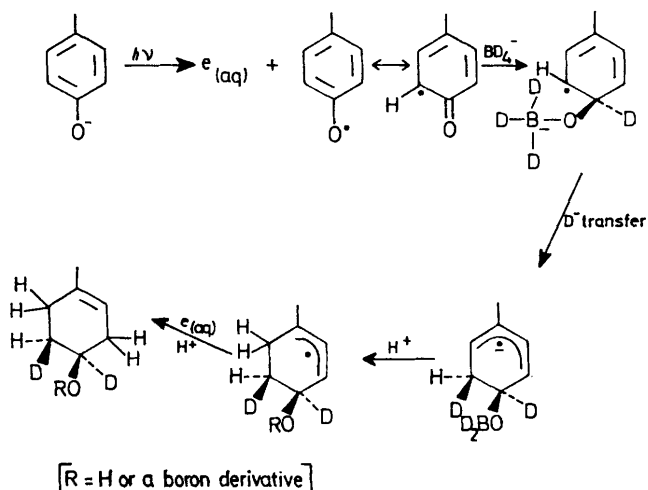


cyclohexenol obtained by irradiating *p*-cresol in NaOD-Na-BH₄-D₂O showed partial incorporation of deuterium at H(2), H(3), H(7), and H(8).

The remarkably stereospecific labelling as in (5) must imply that the transfer of deuterium from BD₄⁻ to C(1) in *p*-cresol occurs before the reduction at the adjacent position and it suggests the intervention of a cyclic mechanism. Since it is known⁵ that electronic excitation of phenoxide ions in aqueous solution generates solvated electrons and phenoxyl radicals, we are led to propose the mechanism in Scheme 2 for the production of 4-methylcyclohexenol.

The intervention of solvated electrons in the process is supported by the observation that the photoreduction is strongly inhibited when conducted under 1 atmosphere pressure of N₂O, a specific scavenger⁶ of solvated electrons.

The 4-methylcyclohexenol seems likely to be a secondary product, for it can be produced by irradiating 4-methyl-



SCHEME 2

cyclohexenol in the presence of phenol and NaBH₄. Mass spectrometric studies of the 4-methylcyclohexanol produced with deuterated reagents indicate that it contains a maximum of 2 hydrogen atoms derived from BH₄⁻ and a minimum of 4 from H₂O.

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