O_{33}

HYDROXYLATION AND BROMINATION OF INDOLINES AND TETRAHYDROQUINOLINE IN SUPERACIDS

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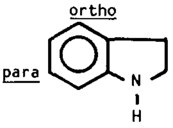
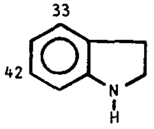
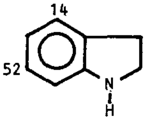
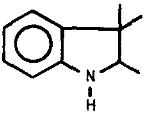
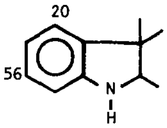
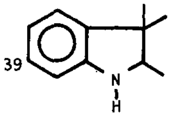
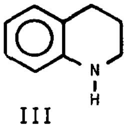
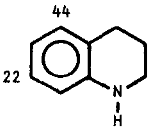
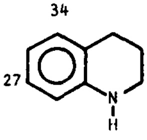
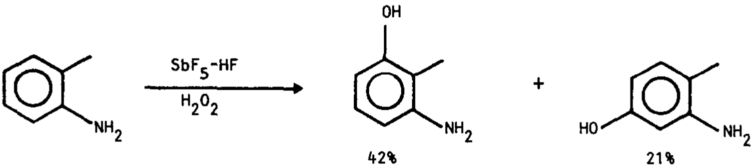
In superacid SbF_5-HF, indolines I and II, and tetrahydroquinoline III are monohydroxylated by hydrogen peroxide and monobrominated by bromine.

SUBSTRATE	HYDROXYLATION position - %	BROMINATION position - %
 I		
 II		
 III		

In the reaction conditions these substrates are reacting as ammonium ions with the electrophile (protonated hydrogen peroxide $H_3O_2^+$ or 'Br^+'). Substitution occurs ortho or para to the alkyl group which is winning out over the deactivating protonated nitrogen.

The brominating agent appears to be more sensitive to steric hindrance than $H_3O_2^+$ (*ortho*/*para* ratio of Br-derivatives < *ortho*/*para* ratio of OH-derivatives).

For a given reaction the observed *ortho*/*para* substitution ratio is higher in the tetrahydroquinoline than in the indoline series and this might be the result of the Mills-Nixon effect (*o*/*p* ratio of hydroxylation is the same on *III* and on *o*-toluidine).



In superacids, protonation protects the nitrogen group from oxidation or degradation and electrophilic substitution occurs at positions normally unreactive in usual conditions.