REACTIONS OF ARYLHYDROXYLAMINES AND RELATED COMPOUNDS WITH BENZENE. AN APPLICATION TO HETEROCYCLIC CHEMISTRY

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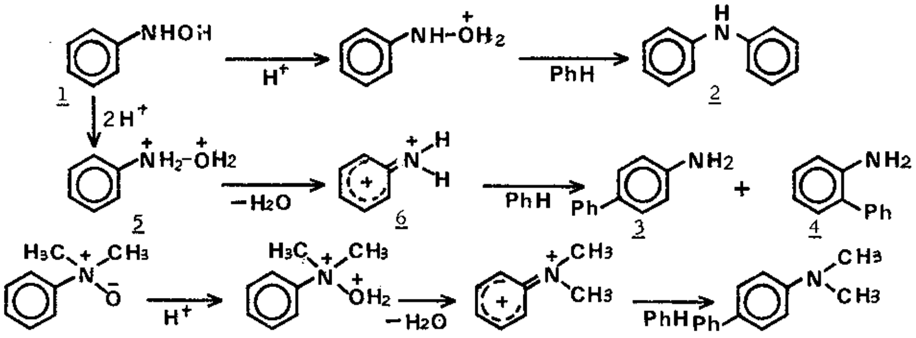
The reaction of arylhydroxylamine with benzene catalysed with trifluoroacetic acid yields diphenylamine. The addition of trifluoromethanesufonic acid changed the reaction site from nitrogen atom to aromatic carbon atoms of arylhydroxylamine, and the major products were aminobiphenyls. Concerning the possible reaction mechanism, we must consider the effect of acidity. Diphenylamine (2) can result from an acid-catalysed S_N type reaction on the nitrogen atom. A possible mechanism leading to aminobiphenyls (3, 4) involves an imoniumbenzenium ion (6) which can be formed from diprotonated phenylhydoxylamine (5). The acid-catalysed reaction of N, N-dimethylaniline N-oxide with benzene may give the evidence for the dication mechanism.



Several reactions were shown as example of the application of the present reactions in the heterocyclic compounds. o-Nitrobiphenyl reacts with benzene under acidic reductive conditions to give phenylcarbazole. N-Phenacylphenylhydroxylamine (7) cyclized intramolecularly to give dibenz(b,d)azepinone (8). By use of an intramolecular N-oxide phenylation, dimethylapoerysopine (10) was prepared.