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INTRAMOLECULAR HOMOLYTIC AMINATION BY N-CHLOROAMINES: NEW SYNTHESES OF INDOLINES AND TETRAHYDROQUINOLINES.

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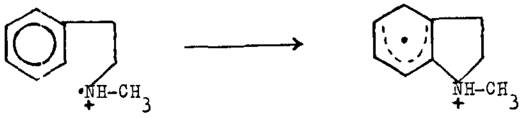
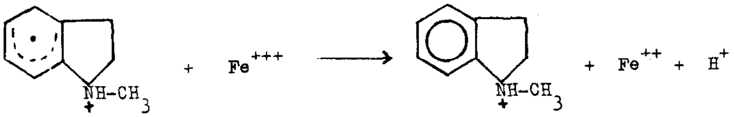
THE homolytic aromatic amination with dialkyl-N-chloroamines and reducing metal salts (Fe^{++},Ti^{+++}) offers a new,large possibility for the study of homolytic aromatic substitutions and an actual synthetic interest.In fact N-chloroamines are readily available,the reaction is carried out easily and rapidly,yields are often good,sometimes excellent (e.g. 92% with methylbenzyl-N-chloroamine and benzene) and the orientation is often selective.Furthermore the reaction applies, in suitable conditions,either to aromatic compounds with strong electron-releasing groups,as anisole and acetanilide,or to compounds with not strongly electron-withdrawing groups,as halobenzenes, benzylic halides and benzyl ethers (1).The bulk of the alkyl groups in N-chloroamines always prevents an extensive attack in ortho positions.

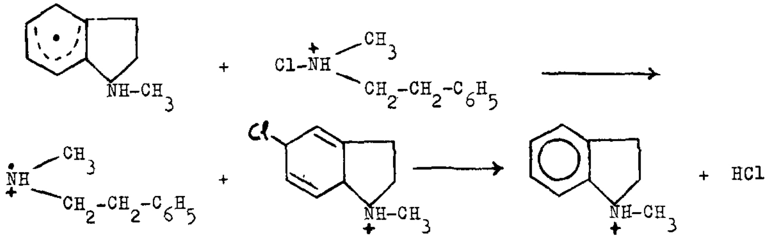
We have now tested the possibility of intramolecular ortho-aminations with methyl-2-phenylethylamine and methyl-3-phenylpropylamine.The corresponding N-chloroamines are quantitatively obtained with solutions of sodium hypochlorite.The reaction of the methylphenylethyl-N-chloroamine and ferrous sulphate in concentrated sulphuric acid is exothermic and very sensitive to the temperature. If the reaction is carried out by adding powdered ferrous sulphate to a 2M solution of the N-chloroamine in sulphuric acid,without cooling,the temperature rises from 0° to 35°C and the products of the reaction are N-methylindoline (13%) and a resinous not basic product. By cooling under -5°C the resinous product disappears and the products of the reaction are N-methylindoline (27%) and benzyl chloride (44%). N-methylindoline is formed, in our opinion, by an intramolecular addition of the amino radical,



and a subsequent oxidation by ferric salt,



and/or by a chain radical addition followed by hydrogen chloride elimination, as some results indicate in the amination of iodobenzene(1[b])



The benzyl chloride can be considered the product of β-scission of the amino radical, analogous to the homolytic scission of alkyl-hypochlorites (2):

$$C_6H_5-CH_2-CH_2-\overset{\bullet}{\underset{+}{N}}H-CH_3 \longrightarrow C_6H_5-CH_2^{\bullet} + CH_2=\overset{+}{N}H-CH_3$$

$$C_6H_5-CH_2^{\bullet} + C_6H_5-CH_2-CH_2-\overset{+}{N}HCl-CH_3 \longrightarrow$$

$$C_6H_5-CH_2-Cl + C_6H_5-CH_2-CH_2-\overset{\bullet}{\underset{+}{N}}H-CH_3$$

The oxidation of the benzyl radical by ferric chloride,

$$C_6H_5\text{-}CH_2\bullet \quad + \quad FeCl^{++} \longrightarrow C_6H_5\text{-}CH_2\text{-}Cl \quad + \quad Fe^{++}$$

is less probable in concentrated sulphuric acid.

The homolytic β-scission is promoted by formation of a benzyl radical;in fact with the methyl-3-phenylethyl-N-chloroamine no β-scission occurs and the N-methyltetrahydroquinoline (kairolin) is formed in much better yield (81%).

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