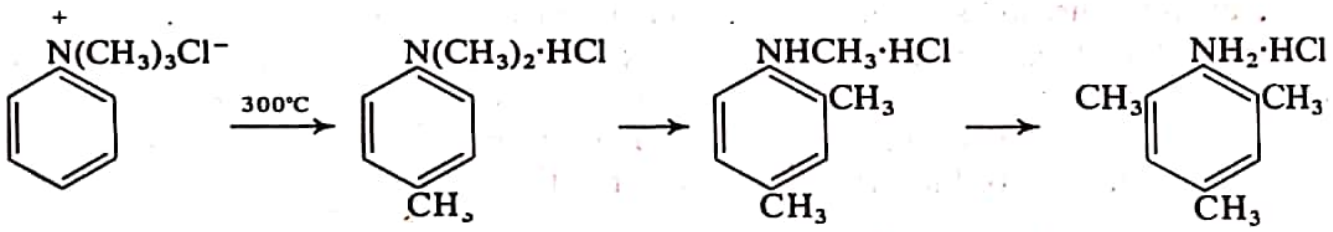
Mono- and dialkylanilines (and the quaternary compounds) as their hydrochlorides (or hydrobromides) undergo rearrangement on strong heating, an alkyl group migrating from the nitrogen atom and entering preferentially the *p*-position or, if this is occupied, the *o*-; *e.g.*, when phenyltrimethylammonium chloride is heated under pressure, the following rearrangement takes place:



This reaction is known as the **Hofmann–Martius rearrangement** (1871); it may be used to prepare aniline homologues.

Many mechanisms have been proposed for the Hofmann–Martius rearrangement. Hughes and Ingold (1952) have proposed the following, based largely on the suggestion of Hickinbottom (1934) that the rearrangement occurs via the formation of an alkyl carbonium ion:

$$C_6H_5\overset{+}{N}H_2C_2H_5Cl^- \rightleftharpoons C_6H_5NH_2 + C_2H_5Cl$$
$$C_2H_5Cl \rightleftharpoons C_2H_5^+ + Cl^-$$
$$C_6H_5NH_2 + C_2H_5^+ \rightleftharpoons C_6H_5NH_3^+ + C_2H_4$$
$$2C_6H_5NH_2 + C_2H_5^+ \rightleftharpoons p\text{-}C_2H_5C_6H_4NH_2 + C_6H_5NH_3^+$$

It should be noted that the heterolytic fission of ethyl chloride is facilitated in the highly polar molten salt.

Rearrangements of this kind have been observed to take place with aniline derivatives of the type $C_6H_5\underset{|}{N}—Z$, where Z is R, X, NH_2, NO or NO_2, *e.g.*,