❖ The von Richter, Sommelet-Hauser, and Smiles Rearrangements

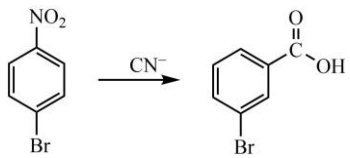
In this section, we will discuss some common types of rearrangement reactions that involve aromatic electrophilic substitution.

➢ *Von Richter Reaction*

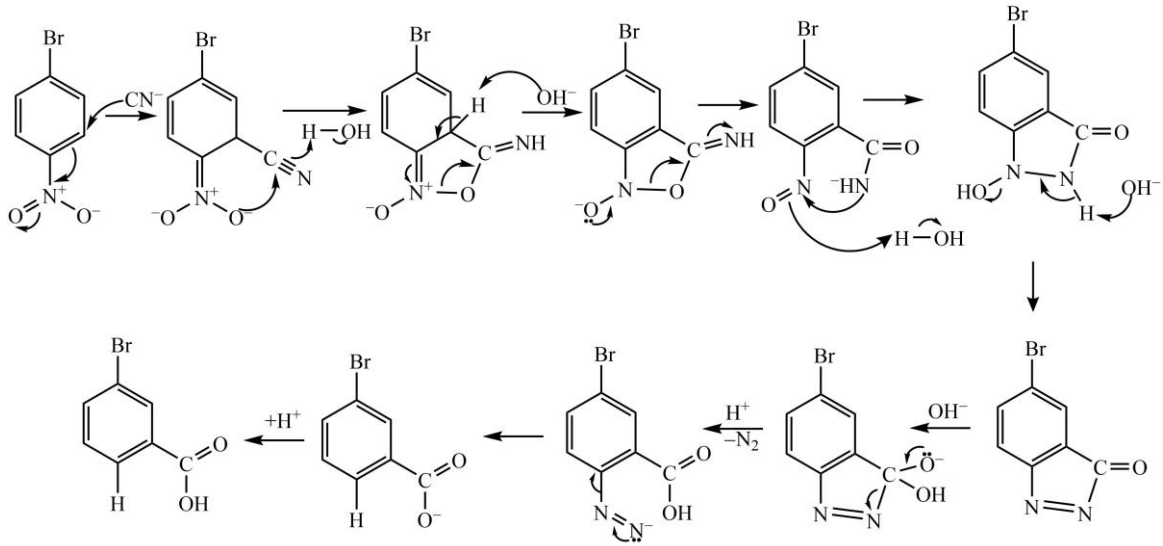
The von Richter reaction may simply be defined as the chemical transformation where aromatic nitro compounds react with KCN in aqueous ethanol to yield cine substitution product by a carboxyl group.

This reaction was invented by a German chemist Victor von Richter in 1871; and therefore, it is also named after him; and It is practically unimportant because of low yield and by-products formation.

Illustrative reaction: Common example is the conversion of *p*-bromonitrobenzene into m-bromobenzoic acid.



Mechanism involved: The most widely accepted mechanism for the von Richter reaction was given by Rosenblum in 1960 when he employed ^{15}N labeling experiments.



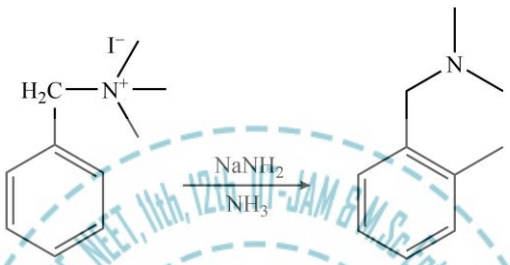
In the first step, the carbon ortho to the nitro group is attacked by cyanide; which is followed by ring-closing through nucleophilic invasion at the cyano group; finally resulting in the rearomatization of the imidate intermediate. The opening of the cycle via nitrogen-oxygen bond-breaking gives rise to an ortho-nitroso benzamide that recyclizes to yield a compound with a nitrogen-nitrogen bond. The elimination of H_2O results in a cyclic azoketone, which undergoes nucleophilic invasion by OH^- to result in a tetrahedral intermediate. This intermediate breakdowns with the removal of the azo group to give an aryldiazene with an o-carboxylate group, which squeezes out dinitrogen gas to be able to have the anionic form of the benzoic acid.

➢ ***Sommelet-Hauser Rearrangement***

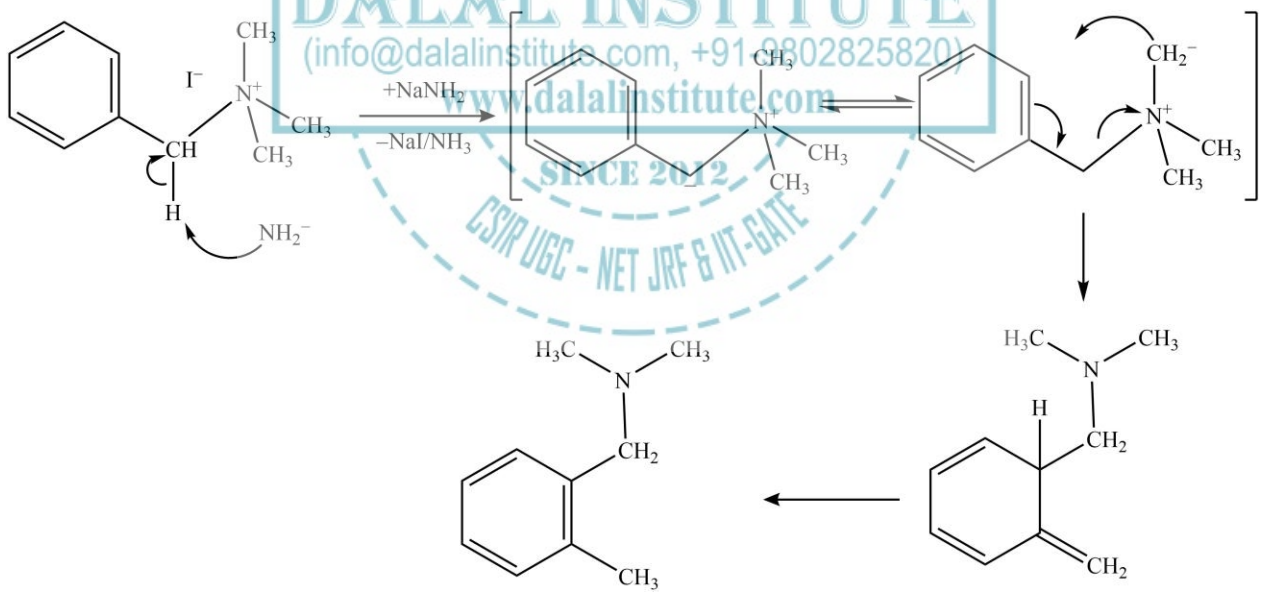
The Sommelet-Hauser rearrangement may simply be defined as the rearrangement reaction of certain benzyl quaternary ammonium salts where the reagent used is sodium amide (or alkali amide) and the reaction results in the N,N-dialkylbenzylamine with a new alkyl substituent in the aromatic o-position.

Now because the final product is a benzylic tertiary amine, it can further undergo alkylation followed by reoccurring rearrangement, and then repeating the process until the blockage of o-site.

Illustrative reaction: The common type of this type of rearrangement is benzyltrimethylammonium iodide that rearranges in the presence of $NaNH_2$ to give the o-methyl derivative of N,N-dimethylbenzylamine.



Mechanism involved: The widely accepted mechanism for the Sommelet-Hauser mechanism is depicted below clear the propagation picture.



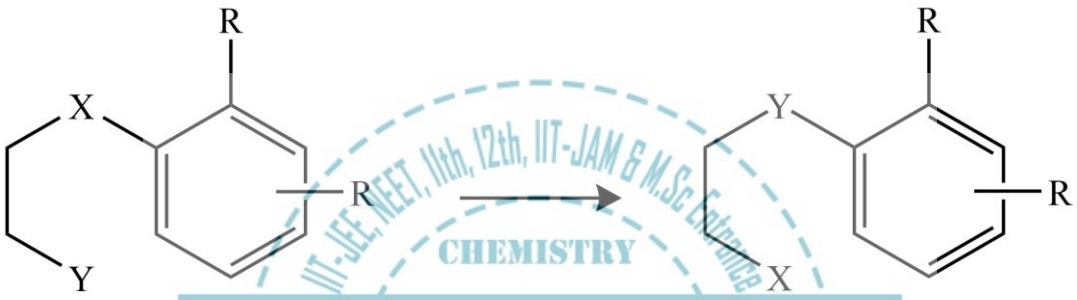
The benzylic methylene hydrogen is acidic and deprotonation occurs to give the benzylic ylide, which is in equilibrium with another ylide formed via deprotonation of one ammonium methyl substituent. Nevertheless, the second ylide is available in much minor quantity, it shows a 2,3-sigmatropic rearrangement as it has a more reactive character than the initial one, and will show subsequent aromatization to give rise to the end product.

➢ *Smiles Rearrangements*

The Smiles rearrangement may simply be defined as an intramolecular aromatic nucleophilic substitution (ArSN) reaction, where the breaking of a C−X single bond and creation of a new C−C or C−X bond take place via ipso substitution.

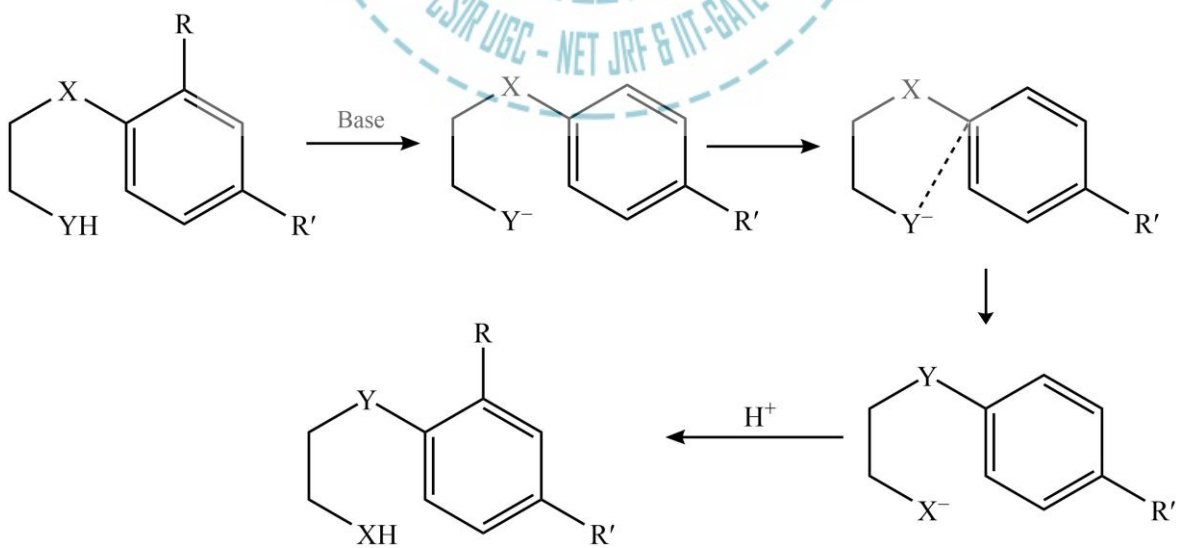
This reaction was invented by a British chemist Samuel Smiles; and therefore, it is also named after him. Its dependence upon leaving group, nucleophile, and the cycle-size of transition state makes it suitable for arene functionalization.

Illustrative reaction: The general reaction showing this type of transformation (Smiles rearrangement) is shown below.



where X represents a sulfide, a sulfone, an ether, or any group capable of displacing from a negatively charged arene. On the other hand, Y represents a group that is capable to act as a strong nucleophile (like alcohol, thiol, or amine).

Mechanism involved: The widely accepted mechanism for the Smiles mechanism is depicted below clear the propagation picture.



Just like other aromatic nucleophilic substitutions, an electron-withdrawing group at ortho position is also required for activation. However, in Truce-Smiles rearrangement, no additional activation is required because the income g nucleophile is enough strong (i.e., organolithium).

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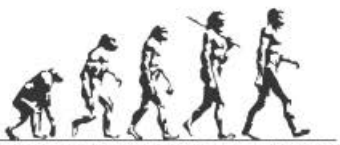

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