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Subject	Chemistry
Paper No and Title	Paper 5: Organic chemistry-II, Reaction Mechanism-I
Module No and Title	Module 35: The Von Richter, Sommelet-Hauser and Smiles rearrangements
Module Tag	CHE_P5_M35

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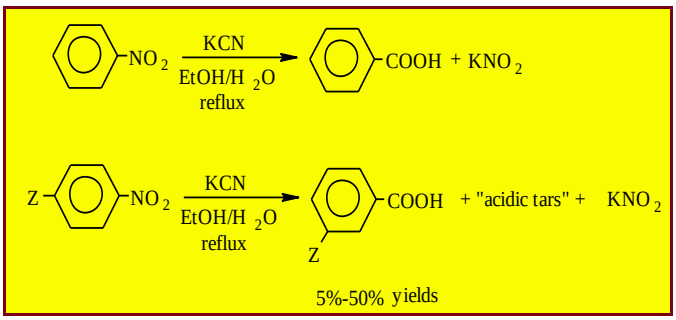
1. Learning Outcomes

After studying this module, you shall be able to

- Know three name reactions *viz.*, Von Richter, Sommelet-Hauser and Smiles rearrangements.
- Learn the various types of rearrangements
- Identify these name reactions
- Understand their reaction mechanisms

2. The Von Richter Reaction

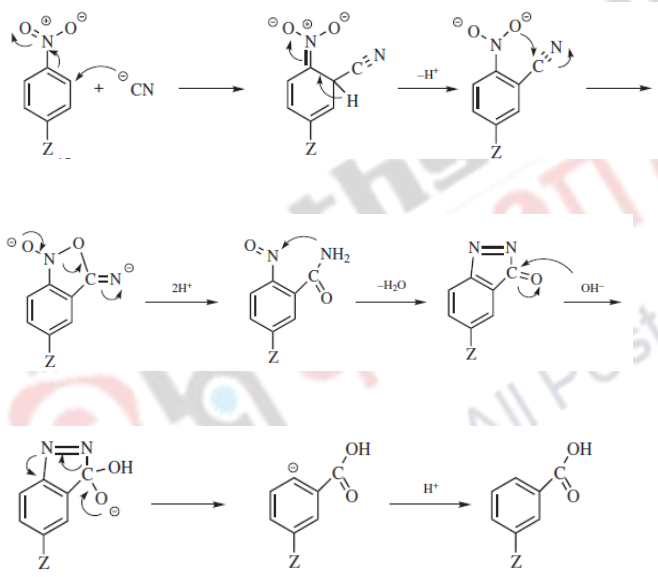
When aromatic nitro compounds are reacted with potassium cyanide to generate a carboxylic acid *ortho* to the existing nitro group is known as **Victor Von Richter reaction** (in 1871). When aromatic nitro compounds are treated with cyanide ion, the nitro group is displaced and a carboxyl group enters with cine substitution, always *ortho* to the displaced group, never *meta* or *para*. The von Richter reaction can be inhibited in the presence of potassium ferricyanide ($K_3Fe(CN)_6$) and sodium sulfite.



As with other nucleophilic aromatic substitutions, the reaction gives best results when electron-withdrawing groups are in *ortho* and *para* positions, but yields are low, usually <20% and never >50%. This reaction has a limited application in organic synthesis.

2.1 Mechanism of Victor Von Richter Reaction

The reaction proceeds through a nucleophilic attack of cyanide ion *ortho* to nitro group followed by intramolecular rearrangement, as shown below:

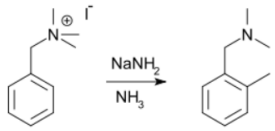


First, the cyanide attacks the carbon-atom in *ortho*-position to the nitro-group. After this the compound regains its aromaticity once again. In the latter step, the negative charged oxygen-atom attack the neighbouring carbon-atom and a five-membered ring is build. It opens under building a carboxylic acid group. Next, another five-membered ring is formed. After a condensation reaction, (resembling Michael reaction) a double bond is built between the two nitrogen-atoms. Elemental nitrogen then leaves the system for

opening the ring. In the last step, the compound is protonated and the 3-halogenbenzoic acid is built.

3. Sommelet-Hauser Rearrangement

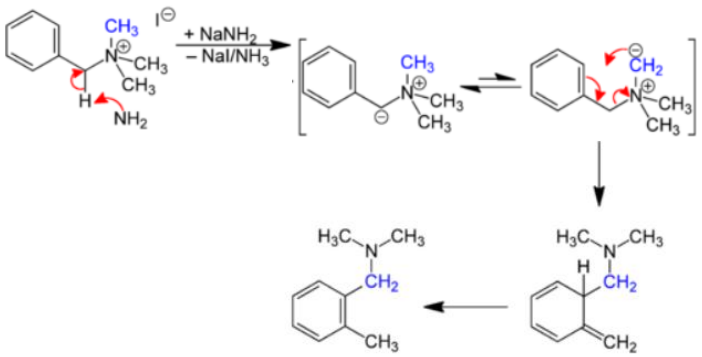
The rearrangement involves the reaction of benzyl quaternary ammonium salts in presence of sodium amide or another alkali metal amide to form N-dialkyl benzyl amine having a new alkyl group in the aromatic *ortho* position is known as **Sommelet–Hauser rearrangement**. The Sommelet-Hauser reaction is highly favored in polar solvents like, NH_3, DMSO, HMPA. Low temperature conditions also favour the reaction.



The product formed benzylic tertiary amine, can further undergo alkylation and the product is again subjected to rearrangement. This process continues until the *ortho* position is blocked. This rearrangement reaction has high yield. It occurs with various types of groups present in the ring. The **Stevens rearrangement** is a competing reaction to the Sommelet Hauser rearrangement.

3.1 Mechanism of Sommelet–Hauser Rearrangement

The reaction proceeds with deprotonation of the benzylic methylene proton which is acidic to yield benzylic ylide. The ylide formed is in equilibrium with the second ylide which is formed by deprotonation of one of the ammonium methyl groups. The second ylide which is present in much smaller amounts undergoes a [2,3] sigmatropic rearrangement and subsequent aromatization in order to form the final product.



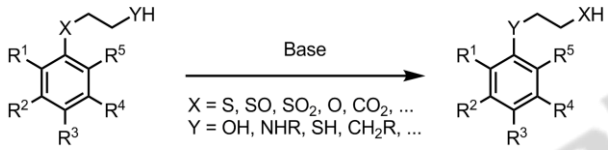
4. Smiles Rearrangement

In 1894, R. Henriques reported that the base treatment of bis-(2-hydroxy-1-naphthyl) sulphide afforded an isomeric compound, 2-hydroxy-2'-mercapto bis-(1-naphthyl) ether. Two decades later, O. Hinsberg carried out a similar set of experiments with the corresponding sulphones, but it was S. Smiles and his co-workers who establishes the structure of the products. Smiles recognised that these set of transformations belonged to separate set of intramolecular nucleophilic aromatic rearrangement, hence the name of the rearrangement.

The **Smiles rearrangement** is an example of intramolecular nucleophilic substitution. It involves attacking on an aromatic system possessing an activating electron-withdrawing group at *ortho*- or *para*-position to the reaction centre connected to a heteroatom. Smiles rearrangement is further involves the migration of an aromatic ring from the heteroatom binding to the reaction center to a more nucleophilic heteroatom.

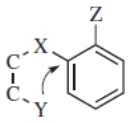
Where, **X** can be a sulfone, a sulfide, an ether or any other substituent which can dislodge from the arene with a negative charge.

The terminal functional group in the chain end *i.e*, **Y** acts as a strong nucleophile for example an alcohol, amine or thiol. In the Smiles rearrangement, the nucleophile Y is generally the conjugate base of SH, SO_2NHR, SO_2NH_2, NH_2, NHR, OH, OR.



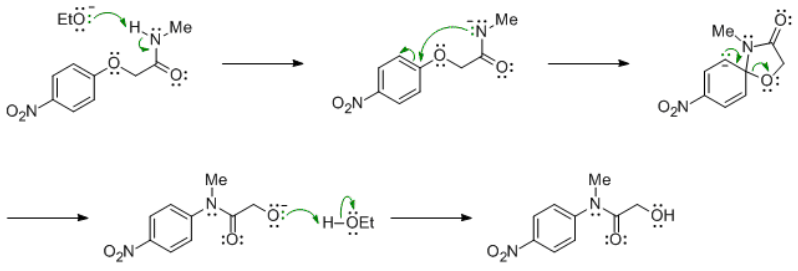
It has been observed that a moderate electron-withdrawing group, preferably in the aromatic *ortho* position, such as chloro and alkoxide can accelerate this rearrangement. On the contrary, the steric hindrance that arises from a substituent at a particular position in the aromatic ring may help in making the rearrangement more facile. The solvent, such as THF has been found to give positive effect and increase the rate of the Smiles rearrangement. This reaction has been thoroughly modified by the use of different ethers as well as various reaction conditions.

4.1 Mechanism of the Smiles Rearrangement



In the following example X = O and Y = N

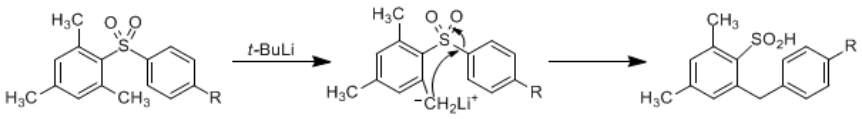
The end group amine after loss of proton acts as a nucleophile and attacks the ring carbon, followed by detachment of the ether oxygen from the ring.



4.2 Truce-Smiles Rearrangement: Modified Smiles Rearrangement

The **Truce-Smiles rearrangement** is an extension of the Smiles rearrangement and this rearrangement involves the migration of an aryl group of diaryl sulfones when treated with a strong base, such as the rearrangement of mesityl *p*-tolyl sulfone to 2-(4-methylbenzyl)-4,6-dimethylbenzenesulfinic acid and the rearrangement of phenyl *p*-tolyl sulfone to *o*-benzylbenzenesulfinic acid. This rearrangement is generally carried out under two distinct conditions: metalation of diaryl sulfones by BuLi in ether and by KOBu*t* in DMSO. Under both conditions, the three isomers of mesityl tolylsulfones give three different products with retention of the tolyl orientations. Furthermore, mesityl β-naphthyl sulfone gives only 5% of rearrangement product under *n*-BuLi/ether conditions.

In the modification known as the **Truce-Smiles rearrangement,** the incoming nucleophile is strong enough so that the arene does not require additional activation The prototypical Truce–Smiles rearrangement requires use of a strong base (such as organolithium) to form the benzylic carbanion that undergoes the rearrangement.

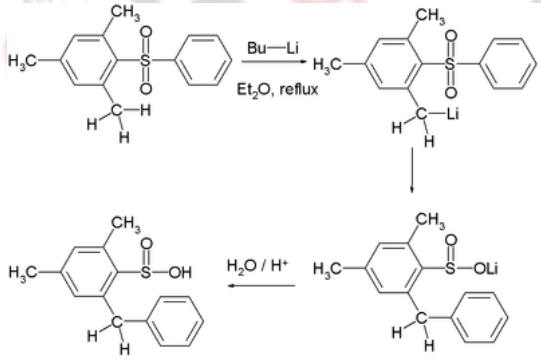


Several other aromatic sulfones undergo a similar rearrangement. The rearrangement of aryl sulfones has been extended to aryl alkyl sulfones. This rearrangement has certain application in the preparation of aromatic sulfinic acids.

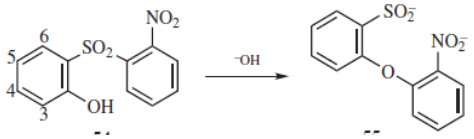
The reaction rate is greatly enhanced by substitution in the 6 position (methyl, chloro, or bromo group) of the attacking ring, for steric reasons. The enhanced rate comes about because the most favorable conformation the molecule can adopt to suit the bulk of the 6-substituent is also the conformation required for the rearrangement. Thus, less entropy of activation is required.

4.3 Mechanism of Truce-Smiles Rearrangement

When sulfone is treated with butyllithium, deprotonation led to the formation of benzylic lithium compound. Truce–Smiles rearrangement and hydrolysis of this intermediate gives the sulfinic acid.



One more example of Truce-Smiles rearrangement is shown below:



5. Summary

- The reaction of aromatic nitro compounds with potassium cyanide to generate a carboxylic acid ortho to the nitro group is known as Victor von Richter reaction.
- The rearrangement reaction of certain benzyl quaternary ammonium salts in presence of sodium amide or another alkali metal amide to form N-dialkyl benzyl amine with a new alkyl group in the aromatic ortho position is known as **Sommelet–Hauser rearrangement**. The Sommelet-Hauser reaction is highly favored in polar solvents like, NH_3, DMSO, HMPA. Low temperature conditions also favour the reaction.
- The **Smiles rearrangement** is an example of intramolecular nucleophilic substitution. It involves attacking on an aromatic system bearing an activating electron-withdrawing group at *ortho*- or *para*-position to the reaction center connected to a heteroatom.
- The **Truce-Smiles rearrangement** is an extension of the Smiles rearrangement and this rearrangement stands for the migration of an aryl group of diaryl sulfones when treated with a strong base, such as the rearrangement of mesityl *p*-tolyl sulfone to 2-(4-methylbenzyl)-4,6-dimethylbenzenesulfinic acid and the rearrangement of phenyl *p*-tolyl sulfone to *o*-benzylbenzenesulfinic acid.