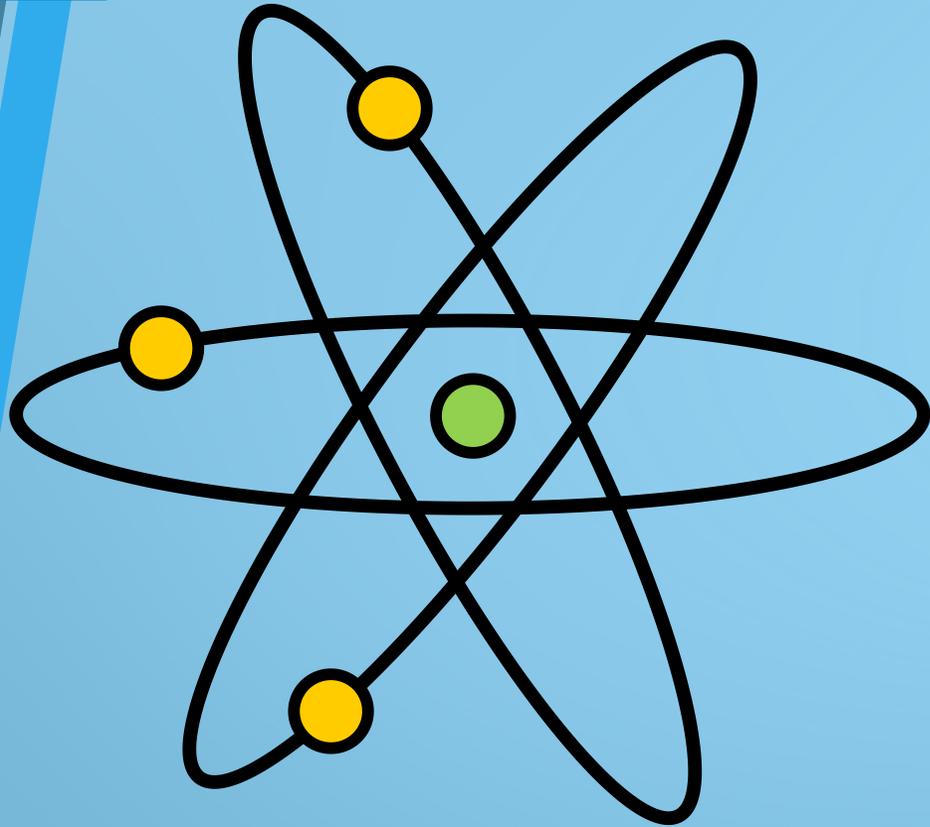


Reimer Tiemann Reaction



Presentation Main Points



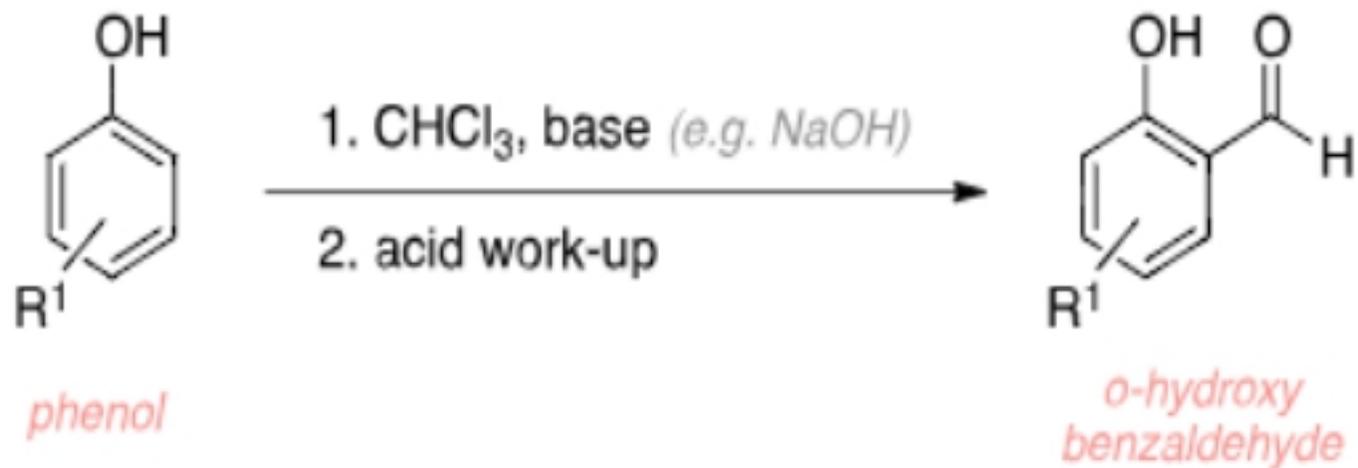
- ✓ **What is Reimer Tiemann Reaction?**
- ✓ **Reimer Tiemann Reaction Details**
- ✓ **Reimer Tiemann Reaction Mechanism**
- ✓ **Scope of Reimer Tiemann Reaction**
- ✓ **References**

What is Reimer Tiemann Reaction?

Reimer Tiemann reaction is a type of substitution reaction, named after chemists Karl Reimer and Ferdinand Tiemann. The reaction is used for the ortho-formylation of C_6H_5OH (phenols).

Reaction: When phenols i.e. C_6H_5OH is treated with $CHCl_3$ (chloroform) in the presence of $NaOH$ (sodium hydroxide), an aldehyde group ($-CHO$) is introduced at the ortho position of benzene ring leading to the formation of o-hydroxybenzaldehyde. The reaction is popularly known as Reimer Tiemann reaction.

A common example of Reimer Tiemann reaction is the conversion of phenol to salicylaldehyde (2-hydroxy benzaldehyde) as shown below.
Reimer Tiemann Reaction



Reimer Tiemann Reaction Details

Since hydroxides are not readily soluble in chloroform, a biphasic solvent system is employed to carry out the reaction. This biphasic solvent system can consist of an aqueous hydroxide solution with an organic phase which contains the chloroform.

These two reagents that are separated are brought together for the reaction to occur. Techniques to bring these two reagents together include – rapid mixing, phase-transfer catalysts or the use of an emulsifying agent.

The reaction is quite effective when other hydroxy-aromatic compounds are used, naphthols for example. Heterocyclic organic compounds that are quite rich in electrons, such as pyrroles and indoles also can undergo the Reimer Tiemann reaction.

The reaction needs heat to initiate the process. However, once the reaction is begun, it can prove to be highly exothermic and further increase the reaction rate. This is the reason why the Reimer Tiemann reaction is prone to thermal runaways.

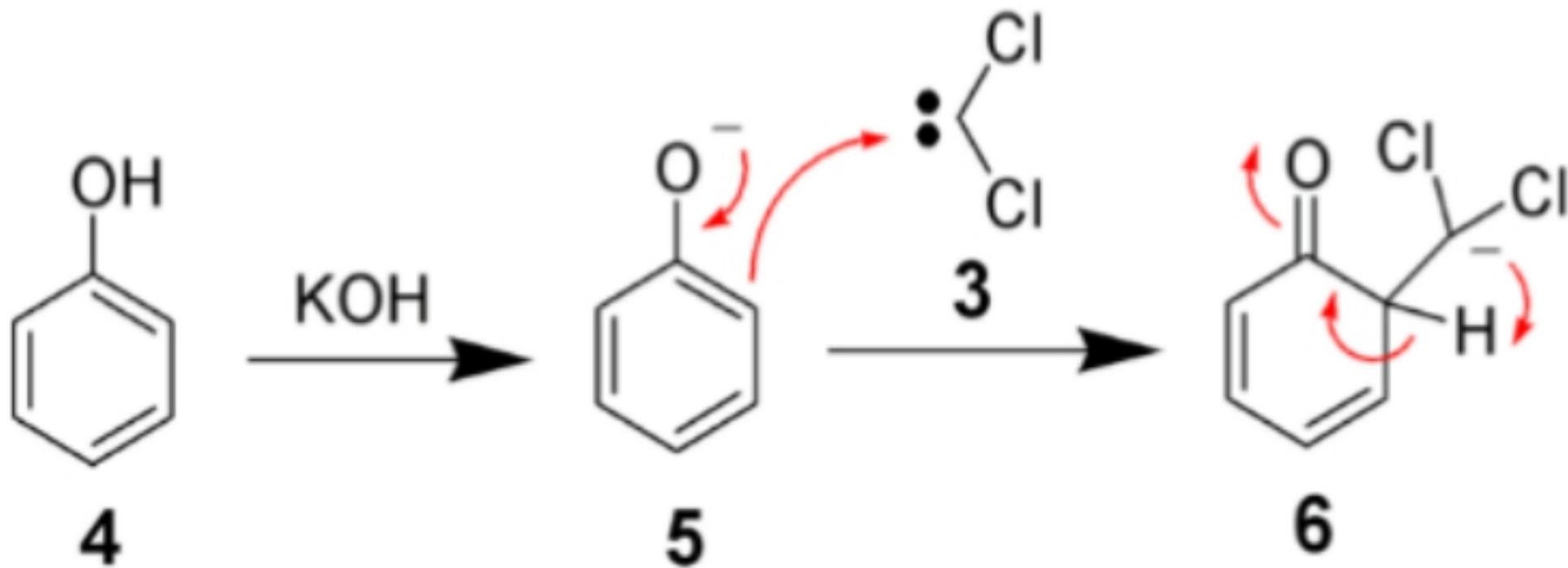
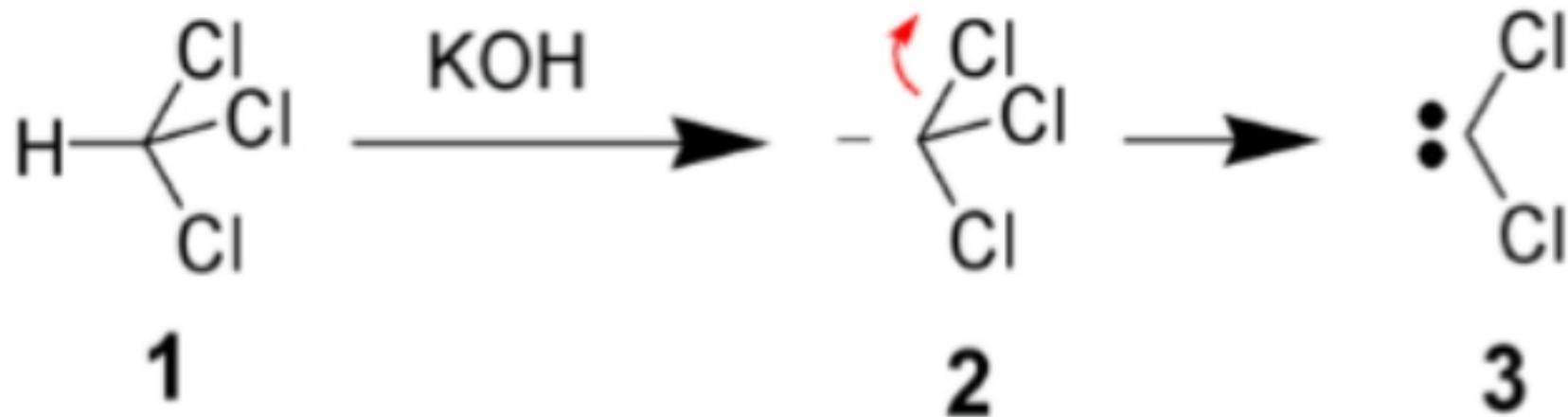
Reimer Tiemann Reaction Mechanism

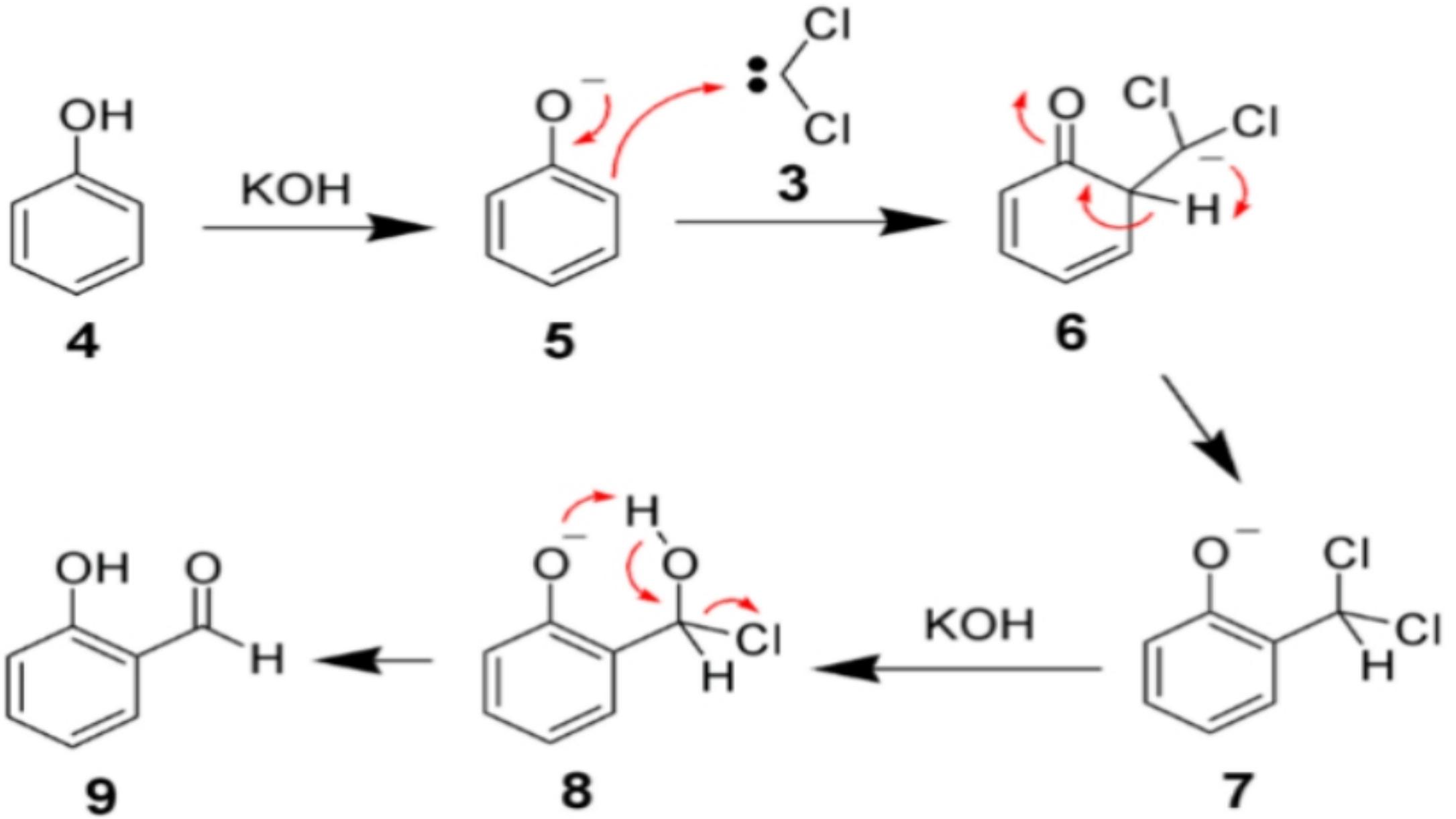
The mechanism of Reimer Tiemann reaction begins with the deprotonation of chloroform by a strong base to form a chloroform carbanion. This chloroform carbanion quickly undergoes alpha elimination and gives rise to dichlorocarbene – the principle reactive species for this reaction.

The Reimer Tiemann reaction is an organic chemical reaction where phenol is converted into an ortho hydroxy benzaldehyde using chloroform, a base, and acid workup. This name reaction can also be described as the chemical reaction used for the ortho-formylation of phenols.

The mechanism of Reimer Tiemann Reaction can be explained in 9 major steps:

- The chloroform is deprotonated by the strongly basic aqueous hydroxide solution, giving the chloroform carbanion.
- This chloroform carbanion readily undergoes alpha elimination, giving dichlorocarbene as the product. As mentioned earlier, the dichlorocarbene is the principle reactive species.
- The aqueous hydroxide also deprotonates the phenol reactant, yielding a negatively charged phenoxide.
- This negative charge is now delocalized into the benzene ring, causing it to be far more nucleophilic.
- This results in a nucleophilic attack on the dichlorocarbene, forming an intermediate dichloromethyl substituted phenol.
- This intermediate is subjected to basic hydrolysis to finally achieve the formation of the desired ortho-hydroxybenzaldehyde.





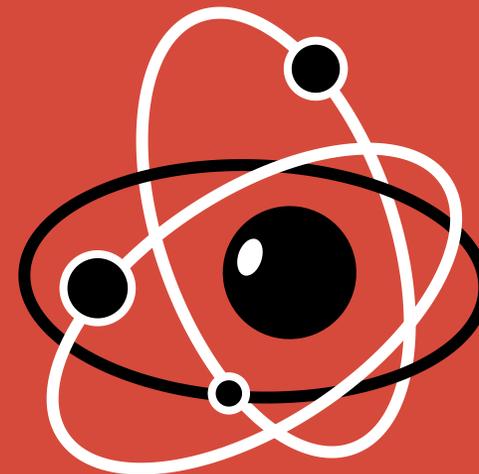
Thus, the given phenol is converted into an ortho-hydroxy benzaldehyde using chloroform, a base and acid workup. It can be noted that the carbene is highly electron-deficient due to the electron-withdrawing nature of its two chlorine groups. This is why it is strongly attracted to the phenoxide which is rich in electrons. The interaction favours ortho-formylation of a selective nature.

Scope of Reimer Tiemann Reaction

The Reimer–Tiemann reaction is effective for other hydroxy-aromatic compounds, such as naphthols. Electron rich heterocycles such as pyrroles and indoles are also known to react.

Dichlorocarbenes can react with alkenes and amines to form dichlorocyclopropanes and isocyanides respectively. As such the Reimer–Tiemann reaction may be unsuitable for substrates bearing these functional groups. In addition, many compounds can not withstand being heated in the presence of hydroxide.

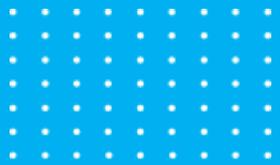
- https://en.wikipedia.org/wiki/Reimer%E2%80%93Tiemann_reaction
- <https://byjus.com/jee/reimer-tiemann-reaction-mechanism/#Reimer-Tiemann-Reaction-Mechanism>
- <https://teamcrusaders.com/site/reimer-tiemann-reaction-and-mechanism-ppt-cdba67>
- <https://brainly.in/question/33801371>
- <https://brainly.in/question/11554953>
- <https://www.quora.com/What-is-the-Reimer-Tiemann-reaction>



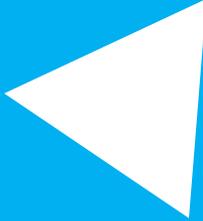
References



Thank You!



Any Question?



Vishwjeet Singh
Pharm D First Year Batch 2020
Amity Institute of Pharmacy,
Lucknow (U.P)

