



Shree H.N.Shukla College of Science Rajkot
B.Sc. (Sem- 3) (CBCS)
CHEMISTRY: [301]
Unit-4 Chapter-6: Name reaction and rearrangement

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Name reaction

A name reaction is a chemical reaction named after its discoverers or developers. Among the tens of thousands of organic reactions that are known, hundreds of such reactions are well-known enough to be named after people. Well-known examples include the Grignard reaction, the Sabatier reaction, the Wittig reaction, the Claisen condensation, the Friedel-Crafts acylation, and the Diels-Alder reaction.

Rearrangement reaction

A rearrangement reaction is a broad class of organic reactions where the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule. Often a substituent moves from one atom to another atom in the same molecule. In the example below the substituent R moves from carbon atom 1 to carbon atom 2:

Intermolecular rearrangements also take place.

A rearrangement is not well represented by simple and discrete electron transfers (represented by curved arrows in organic chemistry texts). The actual mechanism of alkyl groups moving, as in Wagner-Meerwein rearrangement, probably involves transfer of the moving alkyl group fluidly along a bond, not ionic bond-breaking and forming. In pericyclic reactions, explanation by orbital interactions give a better picture than simple discrete electron transfers. It is, nevertheless, possible to draw the curved arrows for a sequence of discrete electron transfers that give the same result as a rearrangement reaction, although these are not necessarily realistic. In allylic rearrangement, the reaction is indeed ionic.

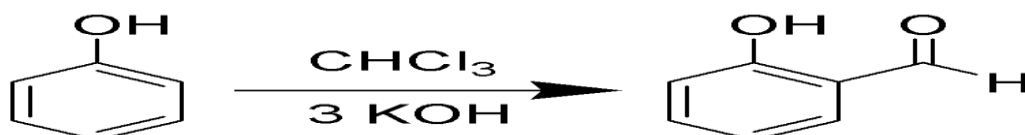
Reimer-Tiemann reaction

The Reimer-Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols; with the simplest example being the conversion of phenol to salicylaldehyde. The reaction was discovered by Karl

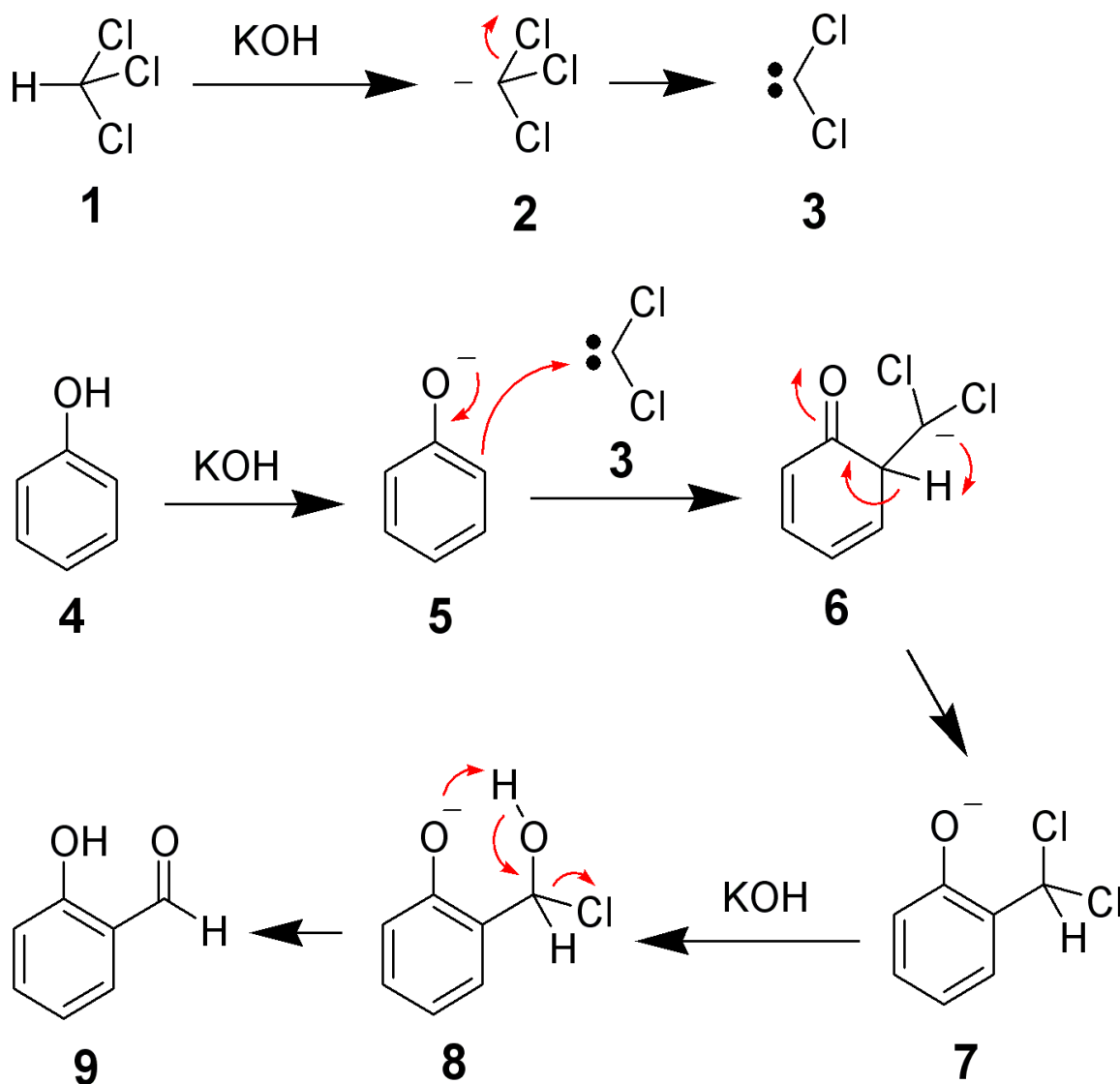


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Reimer and Ferdinand Tiemann. The Reimer in question was Karl Reimer (1845-1883) not the less known Carl Ludwig Reimer (1856-1921).



Mechanism





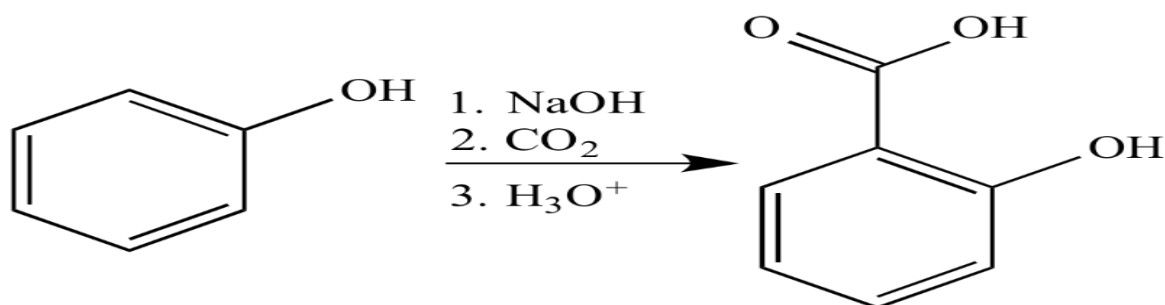
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Question

Sr.no.	Questions	Answer
1	The Reimer–Tiemann reaction is_____ directing group.	Ortho
2	The Reimer–Tiemann reaction convert phenol into	Salicylaldehyde
3	Which reagent is useful to complete reimer tiemann reaction	CHCl ₃ KOH

Kolbe's schmdit

When phenol is treated with sodium hydroxide, phenoxide ion is generated. The phenoxide ion generated is more reactive than phenol towards electrophilic aromatic substitution reaction. Hence it undergoes electrophilic substitution reaction with carbon dioxide which is a weak electrophile. Ortho-hydroxybenzoic acid (salicylic acid) is formed as the major product. This reaction is popularly known as Kolbe's reaction. It is named after the scientist Hermann Kolbe.



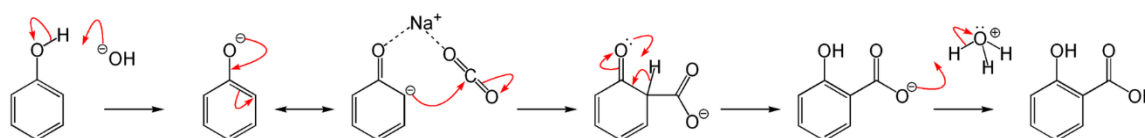
Kolbe's reaction is a carboxylation chemical reaction. This reaction is preceded by allowing sodium phenoxide to absorb carbon dioxide and then heating this



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product at a temperature of 125°C under the pressure of several atmospheres of carbon dioxide. The unstable intermediate formed undergoes a proton shift which leads to the formation of sodium salicylate. The subsequent acidification of the mixture produces salicylic acid.

Mechanism



Question

Sr.no	Question	Answer
1	What is the product of Kolbe's schmdit reaction	Salicylic acid
2	What is the starting material of Kolbe's schmdit reaction	Phenol
3	Which major product formed by the reaction	Ortho hydroxybenzoic acid
4	Which intermediate form during the reaction	Sodium phenoxide



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Carbylamine reaction

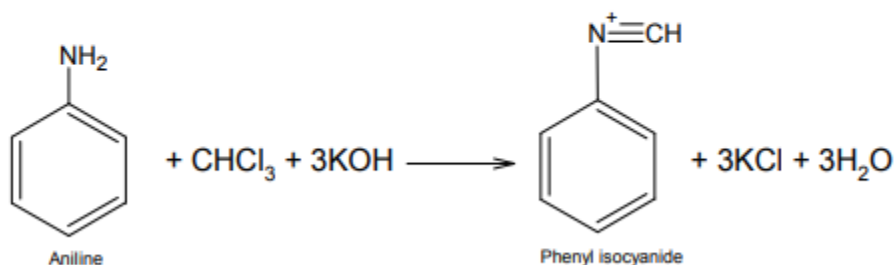
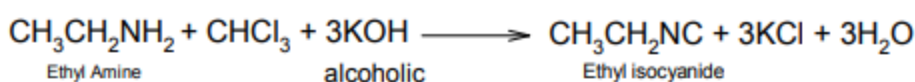
The carbylamine reaction, also known as Hofmann's isocyanide test is a chemical test for

the detection of primary amines. In this reaction, the analyte is heated with alcoholic potassium hydroxide and chloroform.

Carbylamine reaction mechanism includes the addition of amine to the intermediate created from the dehydrohalogenation of chloroform. This intermediate is called dichlorocarbene. The carbylamine reaction is also known as Hofmann isocyanide synthesis. It is the reaction of a primary amine, chloroform and a base to synthesize isocyanides. The dichlorocarbene intermediate is very important for this conversion. The carbylamine reaction cannot be used to synthesize isocyanides from secondary or tertiary amines. In general, the carbylamine reaction can be written as –



Here are a few examples of the carbylamine reaction.





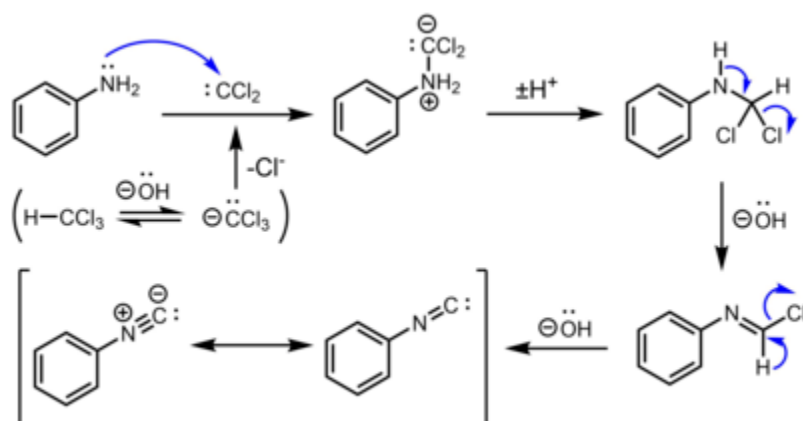
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Hofmann's Isocyanide Test

Since the carbylamine reaction is effective only for primary amines, it can be used as a chemical test for the presence of the presence of primary amines. When used as a test, the carbylamine reaction is also called Hofmann's isocyanide test. In this test, the test substance is heated with chloroform and alcoholic potassium hydroxide. In the case of the presence of primary amine, there will occur a formation of isocyanide (carbylamine) which can be easily identified by its extremely foul smell. The Hofmann isocyanide test does not give a foul odour with secondary or tertiary amines as they do not undergo the carbylamine reaction.

Carbylamine Reaction Mechanism

The first step is the dehydrohalogenation (removal of hydrogen halide from a given substrate) of chloroform to give dichlorocarbene intermediate. This dichlorocarbene intermediate is very reactive. The electrophilic dichlorocarbene attacks the nucleophilic nitrogen of the primary amine. The elimination of the hydrochloric acid leads to the formation of isonitrile. An illustration of the carbylamine reaction mechanism is provided below.



To conclude, the carbylamine reaction can be used to synthesize isocyanides from primary amines with the help of chloroform and a base. The carbylamine reaction can also be employed to test the presence of a primary amine in a given substrate.



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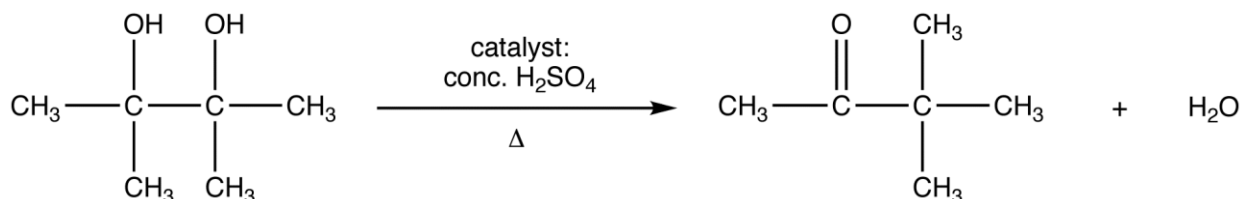
Question

Sr.no	Question	Answer
1	Carbylamine reaction also known as	Hoffmann isocyanide
2	Which intermediate is form during reaction ?	Dichlorocarbene
3	Which amine gives Hoffmann isocyanide test	Only primary amine

Pinacol–pinacolone rearrangement

The pinacol–pinacolone rearrangement is a method for converting a 1,2-diol to a carbonyl compound in organic chemistry. The 1,2-rearrangement takes place under acidic conditions. The name of the rearrangement reaction comes from the rearrangement of pinacol to pinacolone.

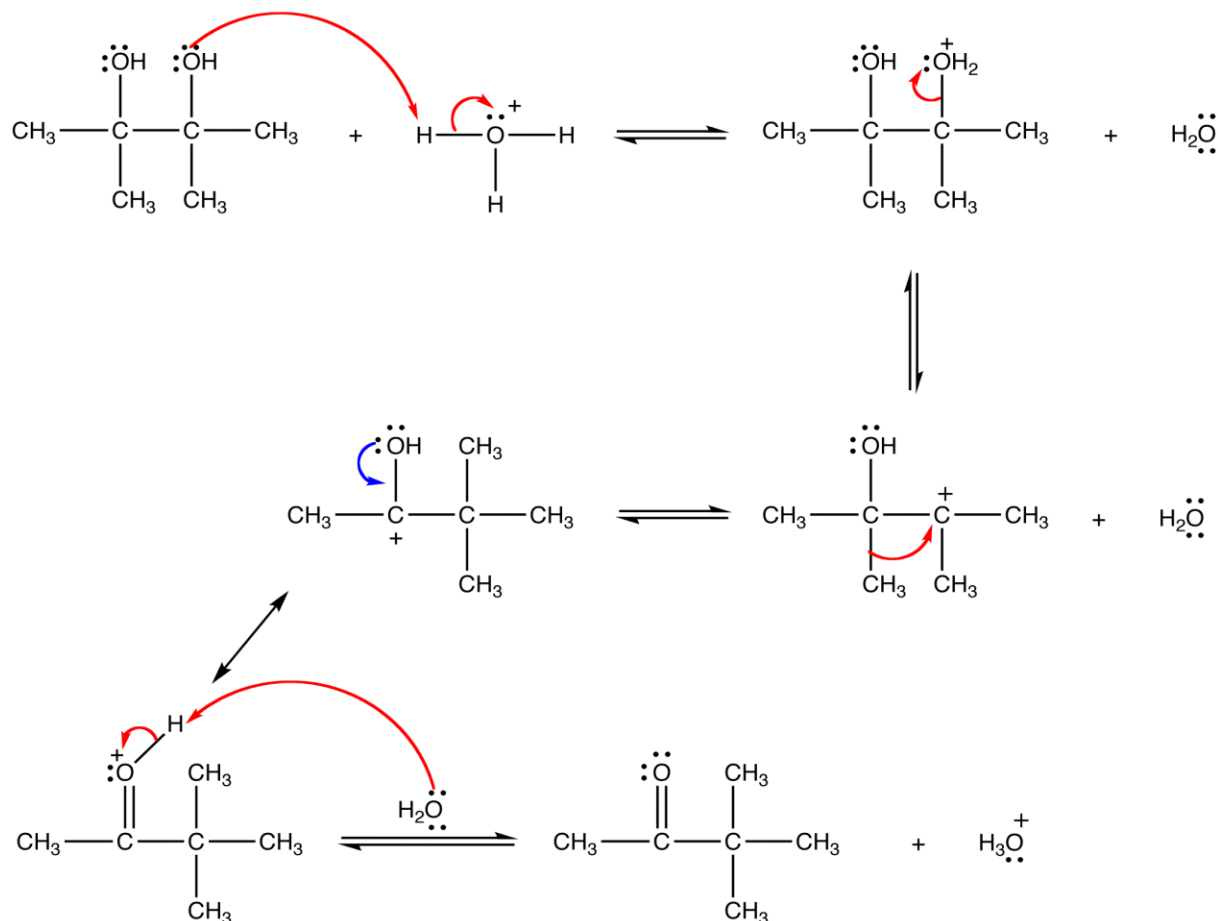
protonation of one of the –OH groups occurs and a carbocation is formed. If both the –OH groups are not alike, then the one which yields a more stable carbocation participates in the reaction. Subsequently, an alkyl group from the adjacent carbon migrates to the carbocation center. The driving force for this rearrangement step is believed to be the relative stability of the resultant oxonium ion, which has complete octet configuration at all centers (as opposed to the preceding carbocation). The migration of alkyl groups in this reaction occurs in accordance with their usual migratory aptitude,





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Mechanism



Question

Sr.no	Question	Answer
1	Which rearrangement is for converting a 1,2-diol to a carbonyl compound ?	Pinacol-pinacolone rearrangement
2	Which intermediate is form during reaction ?	Carbocation
3	Pinacol-pinacolone rearrangement is used for ?	converting a 1,2-diol to a carbonyl compound

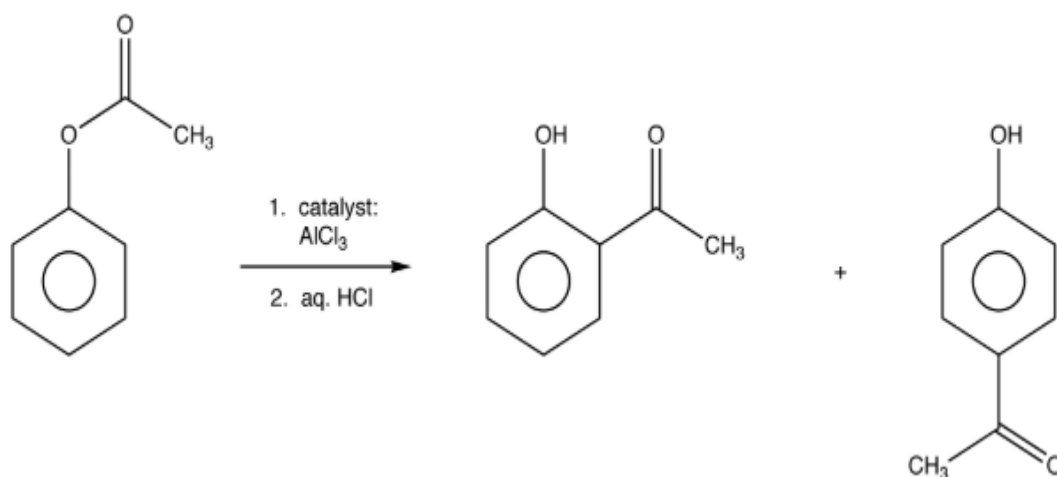


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Fries rearrangement

The Fries rearrangement, named for the German chemist Karl Theophil Fries, is a rearrangement reaction of a phenolic ester to a hydroxy aryl ketone by catalysis of Lewis acids. It involves migration of an acyl group of phenol ester to the aryl ring.

Fries Rearrangement is an organic rearrangement reaction in which an aryl ester is transformed into a hydroxy aryl ketone with the help of a Lewis acid catalyst and an aqueous acid. In this reaction, an acyl group belonging to the phenolic ester migrates to the aryl ring. It is important to note that Fries rearrangement is ortho and para selective, i.e. the acyl group attaches itself at the ortho or para positions of the aryl ring. The selectivity of the reaction can be directed by modifying the reaction conditions (such as the temperature under which the reaction is conducted, or the solvent used in the reaction).



An illustration detailing the Fries rearrangement undergone by phenyl acetate (acetoxyl benzene) is provided above. Note that the products feature ortho and para migrations of the acyl group.



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Fries Rearrangement Mechanism

Initially, the carbonyl oxygen belonging to the acyl group forms a complex with the Lewis acid catalyst (usually AlCl_3). The formation of the complex with the carbonyl oxygen is favoured over the complexation of the phenolic oxygen since the carbonyl oxygen is richer in electrons and is, therefore, a better Lewis base.

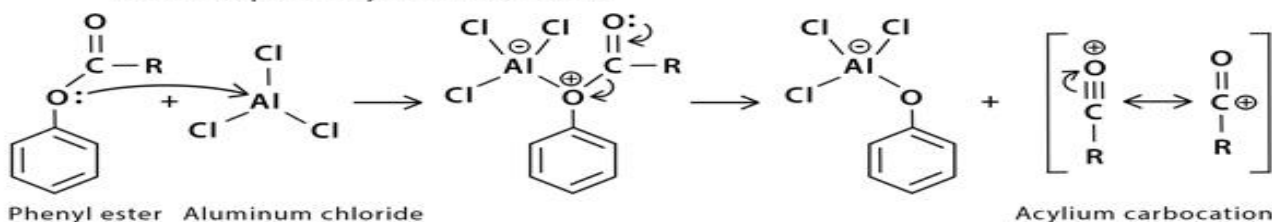
Now, the bond between the phenolic oxygen and the acyl complex becomes polarized, resulting in the rearrangement of the AlCl_3 bond to the phenolic oxygen. This results in the generation of an acylium carbocation.

The acylium carbocation goes on to attack the aromatic ring via an electrophilic aromatic substitution reaction. It is important to note that the orientation of this electrophilic aromatic substitution is temperature-dependent. Low reaction temperatures favour substitutions at the para position and relatively high temperatures favour ortho substitution.

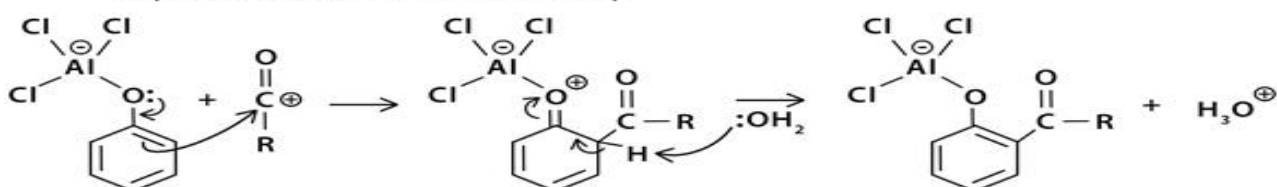
The reaction proceeds through the formation of a carbocation intermediate .

Mechanism of Fries Rearrangement

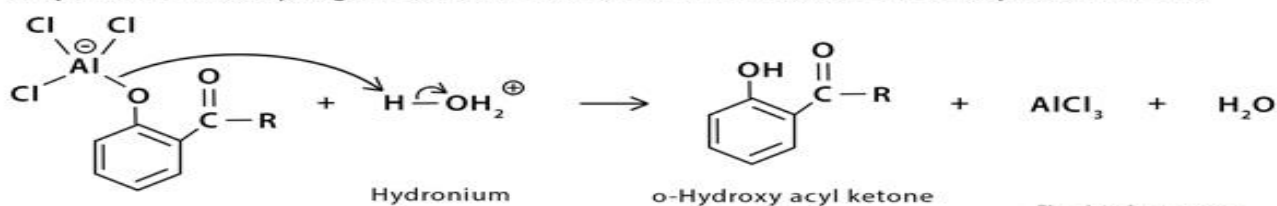
Step 1: Co-ordination of the ester to the Lewis acid followed by rearrangement, resulting in electrophilic acylium carbocation



Step 2: Attack of the alkyl cation via electrophilic aromatic substitution followed by deprotonation to restore aromaticity



Step 3: Acid work up regenerates the Lewis acid and results in the final product (ortho)



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Applications of Fries Rearrangement

Fries rearrangement has the following applications:

Synthesis of o- and p-hydroxy acetophenone, which are useful intermediates in the manufacture of pharmaceuticals

Synthesis of drug and agrochemical intermediates, thermographic materials, and active antiviral agents

The mechanism of the Fries rearrangement reaction is illustrated above. The use of a non-polar solvent in this reaction also favours the formation of orthosubstituted products. Highly polar solvents favour para substitution in this reaction

Question

Sr.no	Question	Answer
1	Fries rearrangement occurs on which position in ring ?	Ortho & para
2	Which lewis acid is used for this rearrangement ?	An. $AlCl_3$
3	Fries Rearrangement is an rearrangement reaction in which an aryl ester is transformed into _____	Hydroxyl aryl ketone

All the best