REARRANGEMENT REACTIONS

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What is Rearrangement Reaction?

The term “rearrangement” is used to describe two different types of organic chemical reactions. A rearrangement may involve the one step migration of an H atom or of a larger molecular fragment within a relatively short lived intermediate.

On the other hand a rearrangement may be a multi step reaction that includes the migration of an H atom or of a larger molecular fragment as one of its steps.

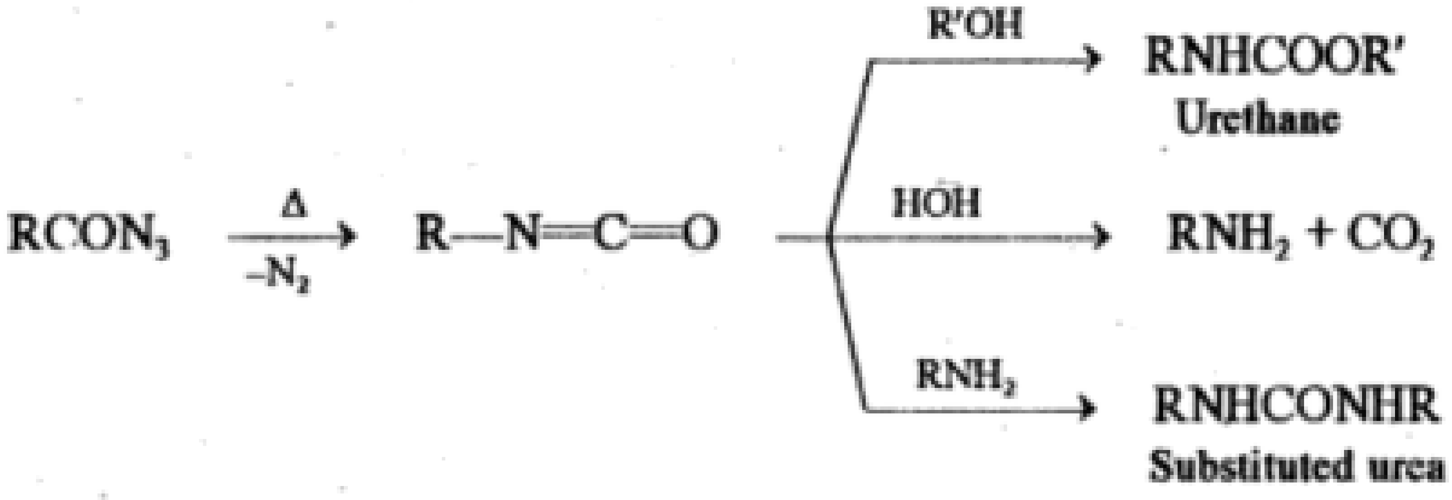
In many rearrangements, the migrating group connects to one of the direct neighbours of the atom to which it was originally attached. Rearrangements of this type are the so-called [1,2] – rearrangements or [1,2] – shifts. These rearrangements can be considered as sigma-tropic processes, the numbers 1 and 2 characterizing the subclass to which they belong.

Curtius Rearrangement

urtius’ reaction involves the heating of an acyl azide which loses nitrogen and then rearranges t
n isocyanate.

$CON_3 \rightarrow R\text{-}N=C=O + N_2$

the reaction is performed in an alcoholic or aqueous medium, the isocyanate further reacts t
rm urethane, amine or substituted urea.



The conversion of acyl azides to isocyanates involves Curtius rearrangement whereas curtius reaction involves the conversion of acids to amines, urethane and substituted urea via Curtius rearrangement.

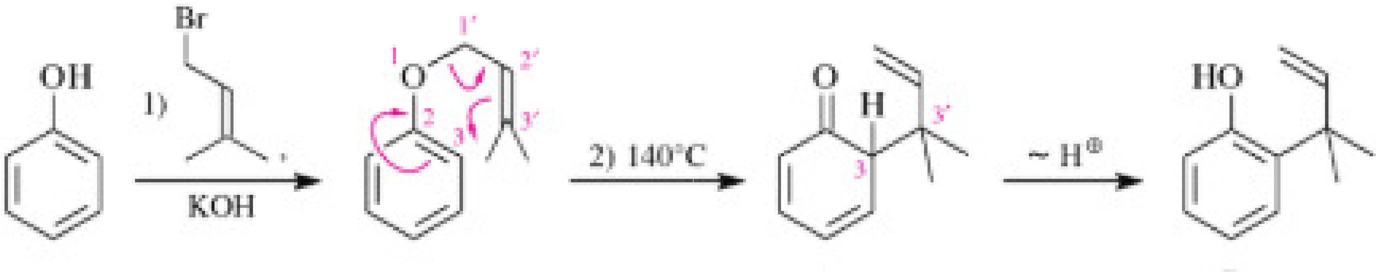
Acyl azide required for the reaction is obtained as follows.

$RCOCl + NaN_3$ (Sodium azide) → $RCON_3$ (Acyl azide) + NaCl

$RCOOC_2H_5$ → $RCONHNH_2$ (Acyl hydrazide) → $RCON_3 + 2H_2O$

Claisen Rearrangement

he classical claisen rearrangement is the first and slow step of the isomerization of allyl aryl thers to ortho allylated phenols. A cyclohexadienone is formed in the actual rearrangement step hich is a [3,3]-sigmatropic rearrangement. Three valence electron pairs are shifted multaneously.
yclohexadienone, a non-aromatic compound, cannot be isolated and tautomerizes immediately o the aromatic and consequently more stable phenol.

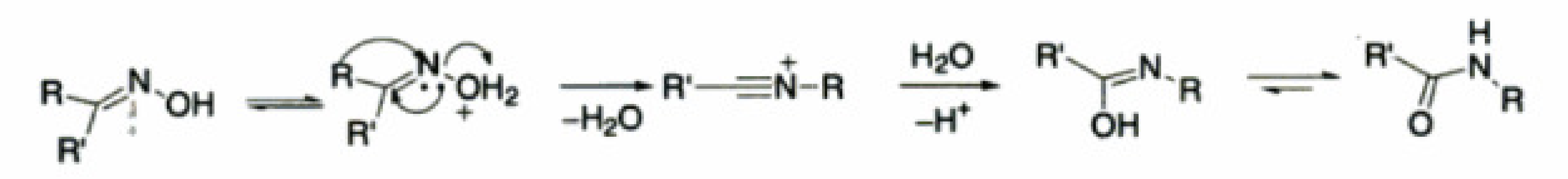


The claisen rearrangement is a thermal rearrangement of allyl aryl ethers and allyl vinyl ethers espectively. It may be regarded as the oxa-version of the closely related cope rearrangement. Claisen has discovered this reaction first on allyl vinyl ethers and then extended to the earrangement of allyl aryl ethers to yield o-allylphenols.

Beckmann Rearrangement

he Beckmann rearrangement , an oxime is converted to an amide . An oxime is easily obtained treatment of aldehyde or ketone with hydroxylamine. The OH group of ketoximes can become a ving group. The Beckmann rearrangement of cyclic oximes results in lactams.

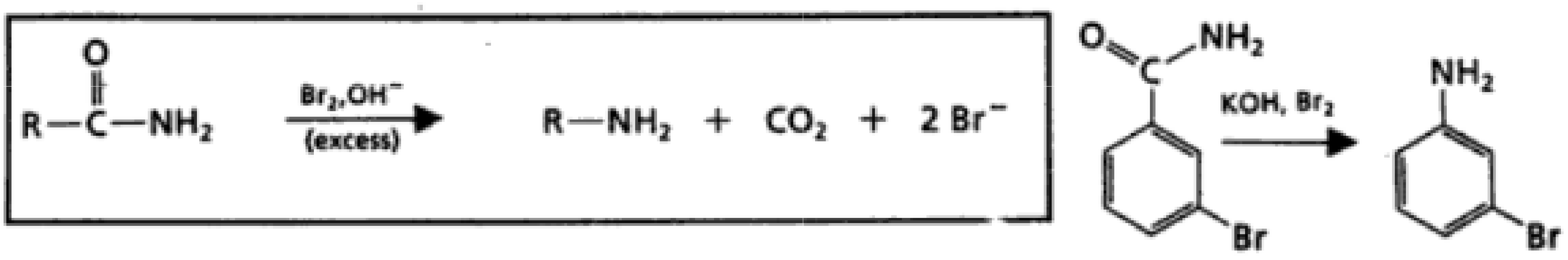
comparison of the structure of the starting ketone with those of the products reveals that the nbination of oxime formation and Beckmann rearrangement accomplishes the insertion of an group between the carbonyl carbon and the alpha carbon.



eckmann rearrangement of the oxime of cyclohexanone is carried out on a very large sca dustrially because the product, caprolactam, is the direct precursor of nylon 6, a versatile polym at has many applications: for example, the manufacture of fibres for carpeting and other textile oncentrated sulphuric acid is used as both the acid catalyst and the solvent for the reaction.

Hofmann Rearrangement

e Hofmann rearrangement results from the treatment of a primary amide with bromine and
droxide ion in water, ultimately forming an amine in which the carbonyl group of the starting
nide has been lost.



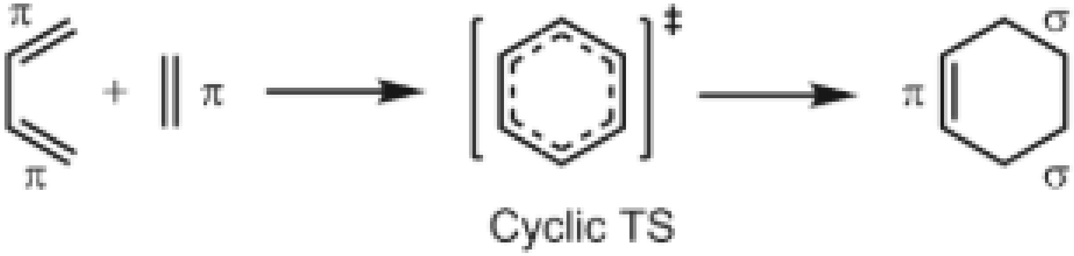
us, the Hofmann rearrangement results in a shortening of the carbon chain by one atom and a
ange in functional group from an amide to an amine. The Hofmann rearrangement occurs
rough a pathway similar to that for the Beckmann rearrangement.

Pericyclic Rearrangement

ricyclic reactions are defined as the reactions that occur by a concerted cyclic shift of electrons. Th finition states two key points that characterize a pericyclic reaction.

rst point is that reaction is concerted. In concerted reaction, reactant bonds are broken and product bonc e formed at the same time without intermediates.

econd key point in pericyclic reactions involves a cyclic shift of electrons. The word pericyclic means arour e circle. Pericyclic words come from the cyclic shift of electrons. Pericyclic reactions thus are characterized b cyclic transition state involving the pi bonds.



ne energy of activation of pericyclic reactions is supplied by heat or by UV light. Pericyclic reactions a ereospecific and it is not uncommon that the two modes of induction yield products of opposi ereochemistry.

Three features of any pericyclic reaction are intimately interrelated. These are:

- ***Activation –*** Pericyclic reactions are activated either by thermal energy or by UV light. However, many reactions that require heat are not initiated by light and vice versa.

- The number of pi bonds involved in the reaction.

- The stereochemistry of the reaction

Photochemical rearrangements

Many photoreactions are known to interconvert isomeric compounds. The term "***rearrangement***" is more eneral than "isomerization" but for the reactions under photochemical rearrangement will not be concerne with a distinction between these terms.

or convenience, we shall classify primary photochemical rearrangements as the following types.

.Cis trans isomerization

.Sigmatropic rearrangements

.Electrocyclic rearrangements

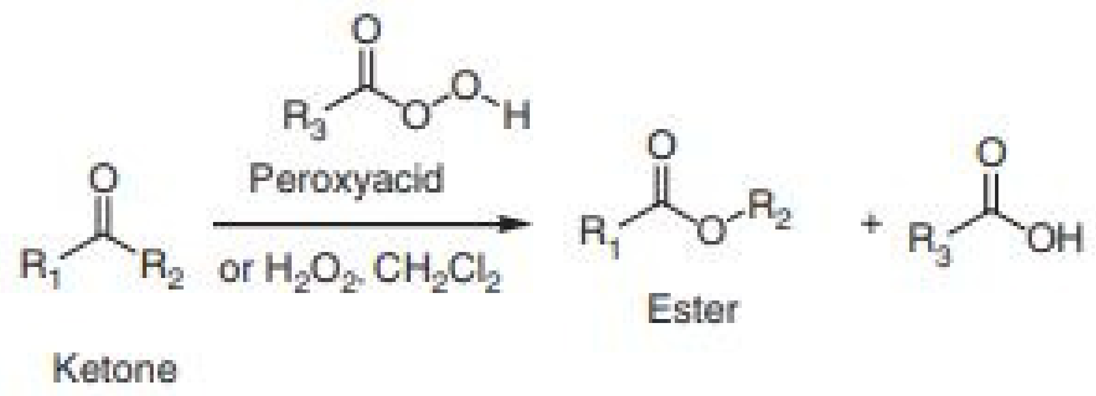
.Structural rearrangements which result from intramolecular cycloadditions.

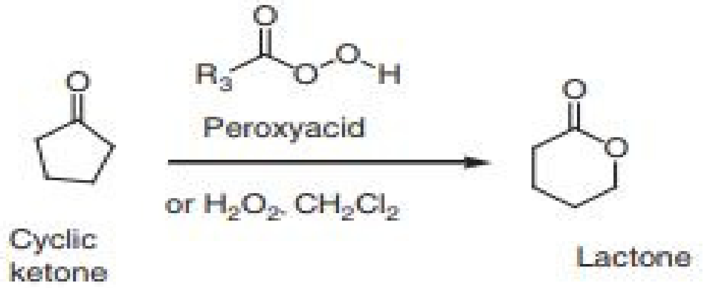
n a broad sense, all four of these classes are special cases of pericyclic rearrangements and for concerted eactions, they all may be treated under a unifying framework guided by the rules derived from orbital ymmetry considerations.

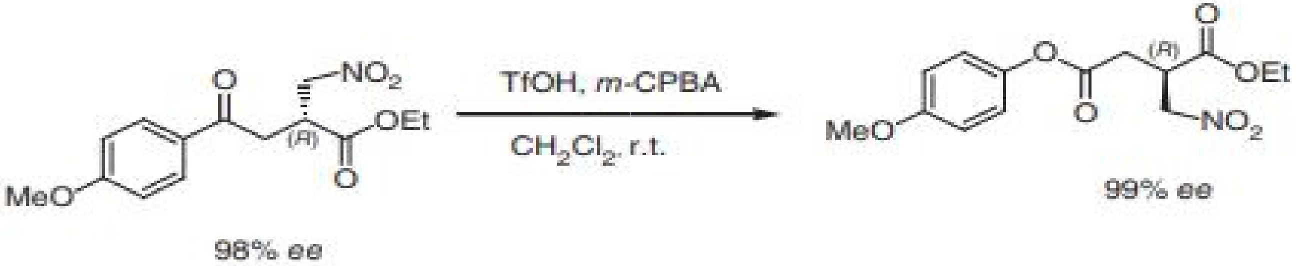
Baeyer–Villiger Oxidation or Rearrangement

he Baeyer–Villiger oxidation is an organic reaction that converts a ketone to an ester or a cyclic ketone to a lactone i
ne presence of hydrogen peroxide or peroxy acids. The reaction was discovered in 1899 by Adolf von Baeyer and
ictor Villiger. It is an intramolecular anionotropic rearrangement where an alkyl group migrates from the carbonyl
arbon atom (migration origin) to an electron-deficient oxygen atom (migration terminus). The most electron-rich
lkyl group (most substituted carbon) that is able to stabilize a positive charge migrates most readily.

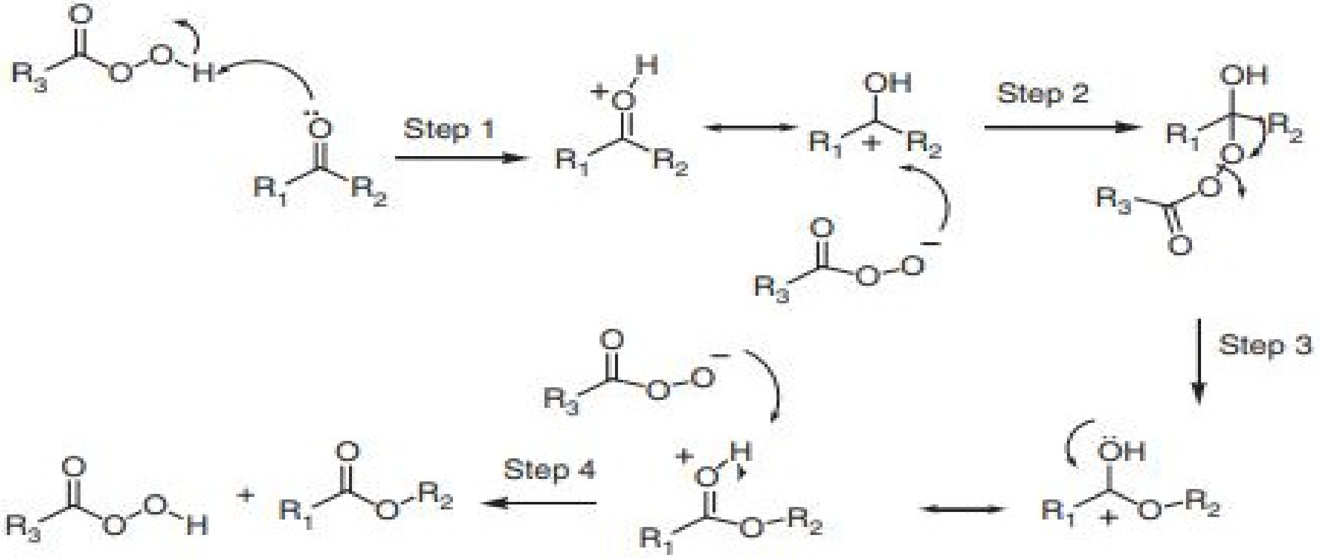
he migration order is as follows: Tertiary alkyl>cyclohexyl>secondary alkyl>phenyl>primary alkyl>CH3 >




Peroxyacid
or H2O2, CH2Cl2
Cyclic ketone
Lactone

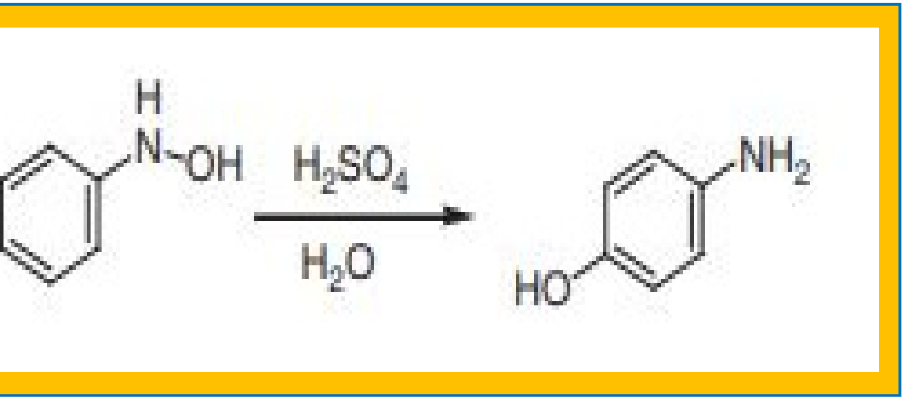

TfOH, m-CPBA
CH2Cl2, r.t.
98% ee
99% ee

Mechanism

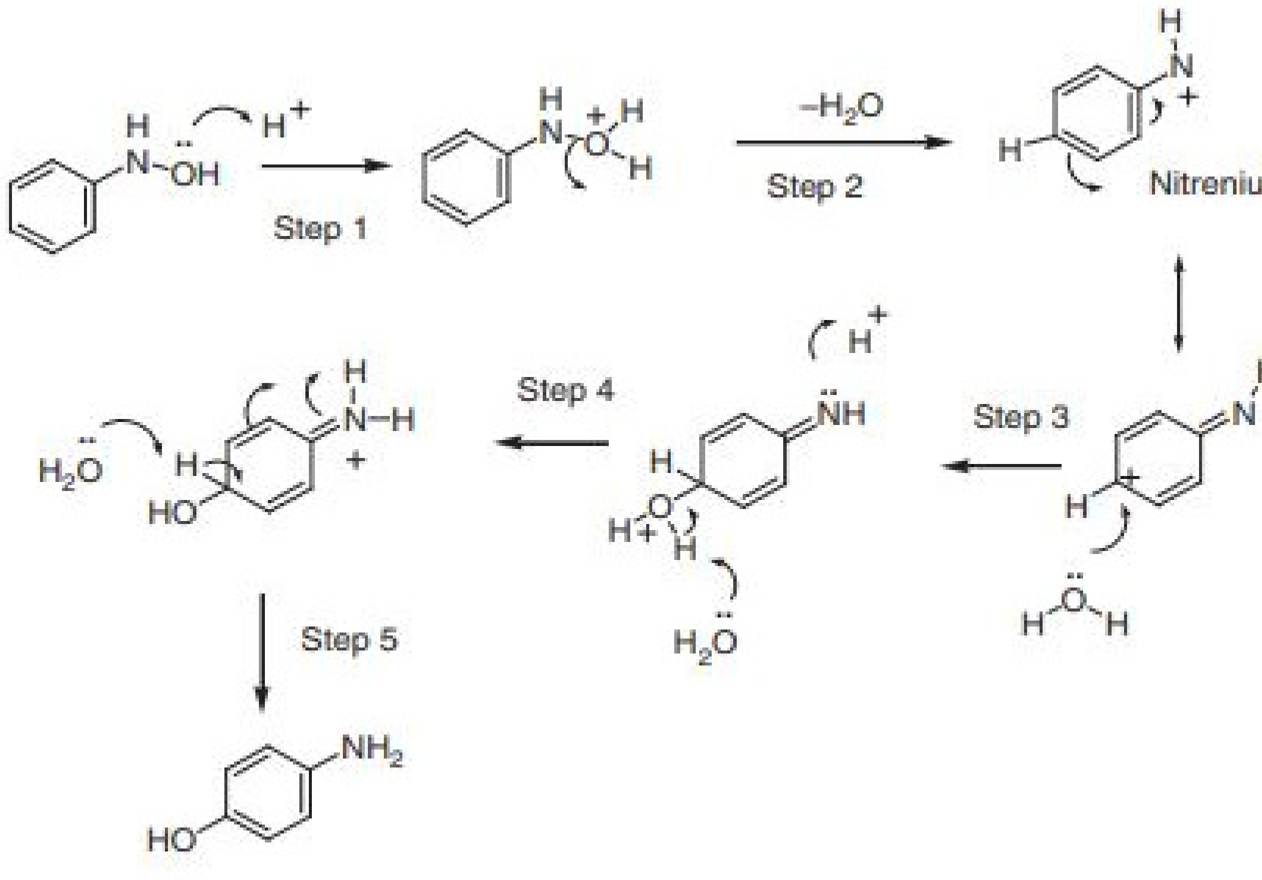

Step 1
Step 2
Step 3
Step 4

Bamberger Rearrangement

he Bamberger rearrangement is an organic reaction used to convert N-phenylhydroxylamine to 4
minophenol in the presence of strong aqueous acid. The reaction is named after German chemist Euge
amberger. Several new catalysts have been developed for the preparation of 4-aminophenol fror
irectly nitrobenzene.

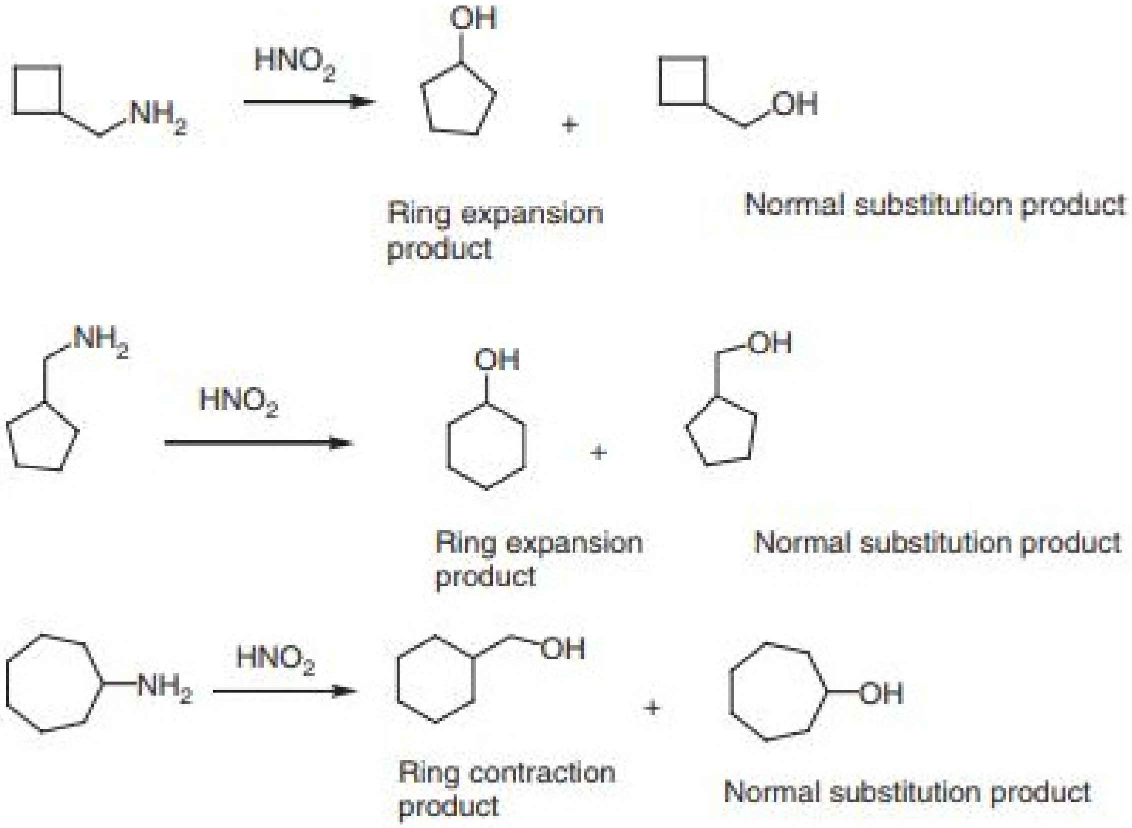


Mechanism



Demjanov Rearrangement

he Demjanov rearrangement is an organic reaction of primary amine with nitrous acid to for
earranged alcohols. The reaction proceeds via diazotization followed by ring expansion or rin
ontraction. The reaction is named after the Russian chemist Nikolay Yakovlevich Demjanov wh
iscovered it in 1903. Several improvements and mechanistic studies have been developed on th
eaction.

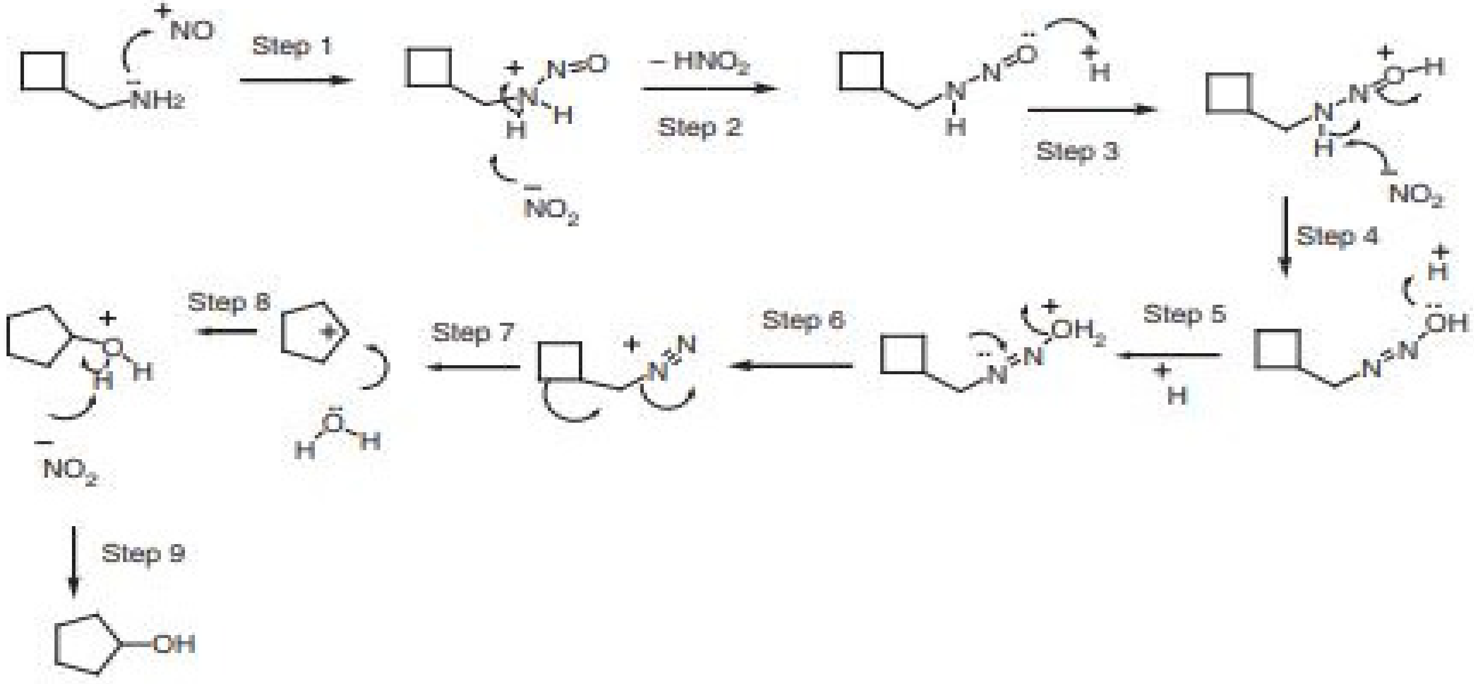


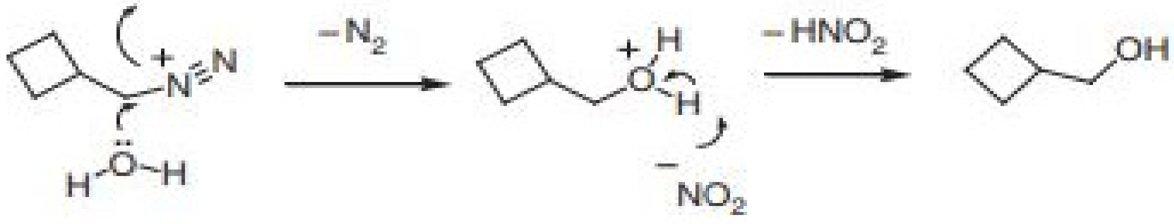
Mechanism

Generation of Nitrosonium Ion

$HNO_2 \rightleftharpoons H^+ + NO_2^-$

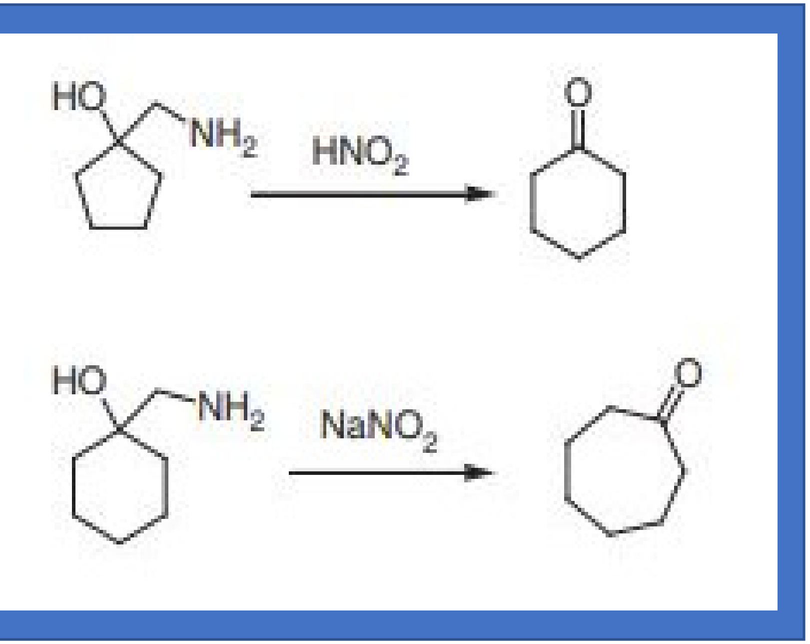
$$H{-}O{-}N{=}O \xrightleftharpoons{H^+} H{-}\overset{+}{\underset{H}{O}}{-}N{=}O \rightleftharpoons H_2O + \overset{+}{N}O$$





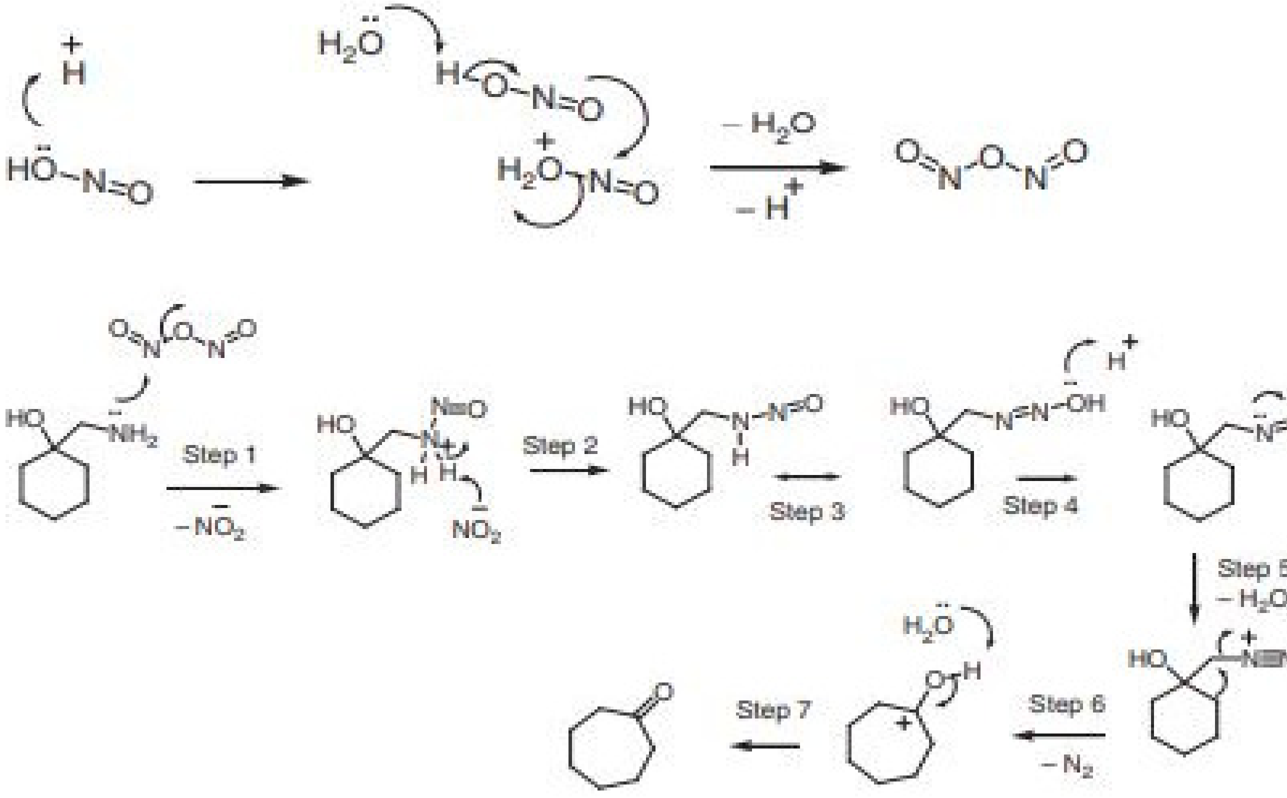
Tiffeneau–Demjanov Rearrangement

e carbocation rearrangement of β-amino alcohol (1-aminomethylcycloalkanol) with nitrous acid to form a ri arged cycloketone is known as the Tiffeneau–Demjanov rearrangement. The ring sizes from cyclopropane looctane can undergo this reaction with ring expansion, although ideal ring size 5–7 provides good yield.



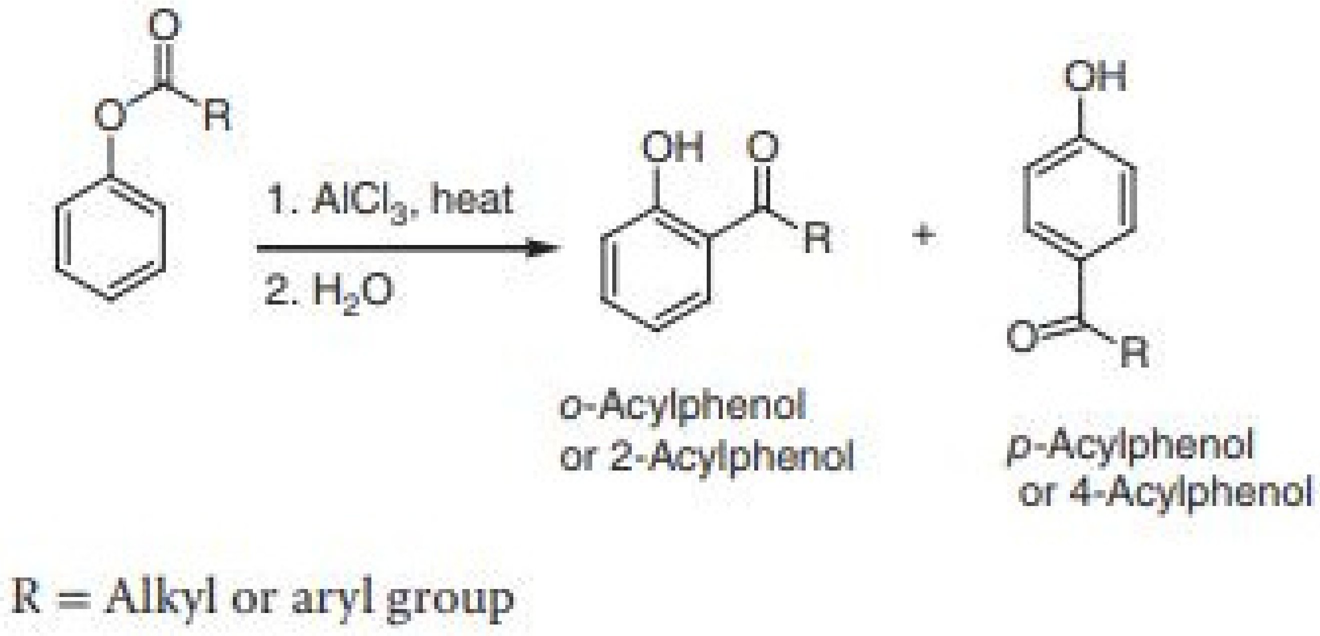
Mechanism

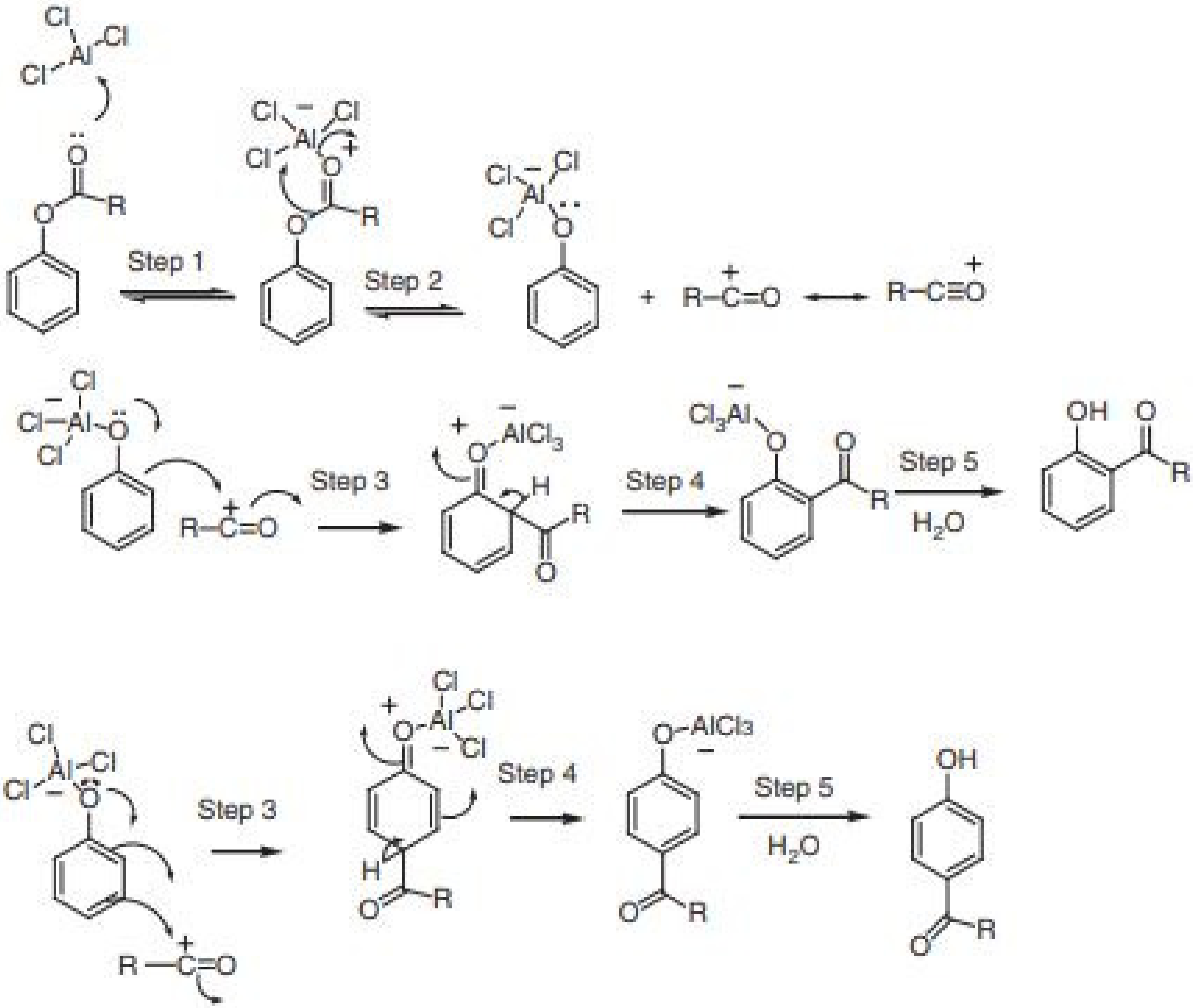
Generation of N_2O_3



Fries Rearrangement

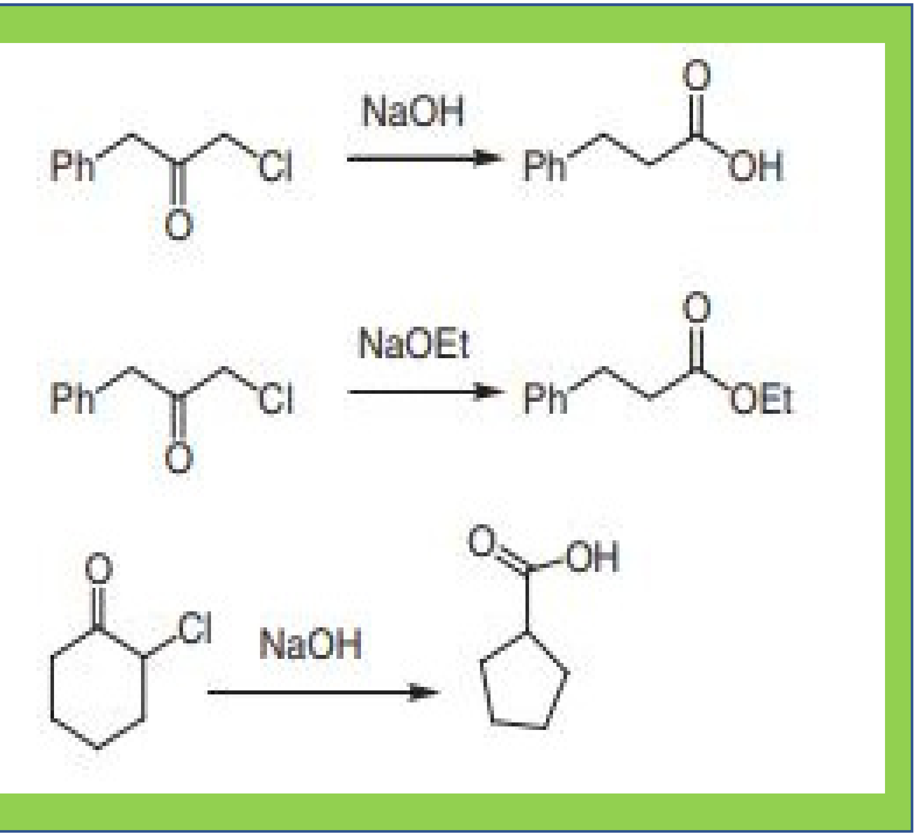
ostly $AlCl_3$, BF_3, $TiCl_4$, or $SnCl_4$ catalysed rearrangement of phenolic esters to 2-hydroxy aryl ketone or 4-hydroxy a one is called the Fries rearrangement, named after the German chemist Karl Theophil Fries. The rearrangement c ceed with other acids such as HF, CF_3CO_2H, and $MeSO_3H$ in an inert solvent or without any solvent. The acids nerally required in excess of the stoichiometric amounts, particularly with the Lewis acids (most common is $AlCl_3$) si y form complexes both with the starting materials and the products.

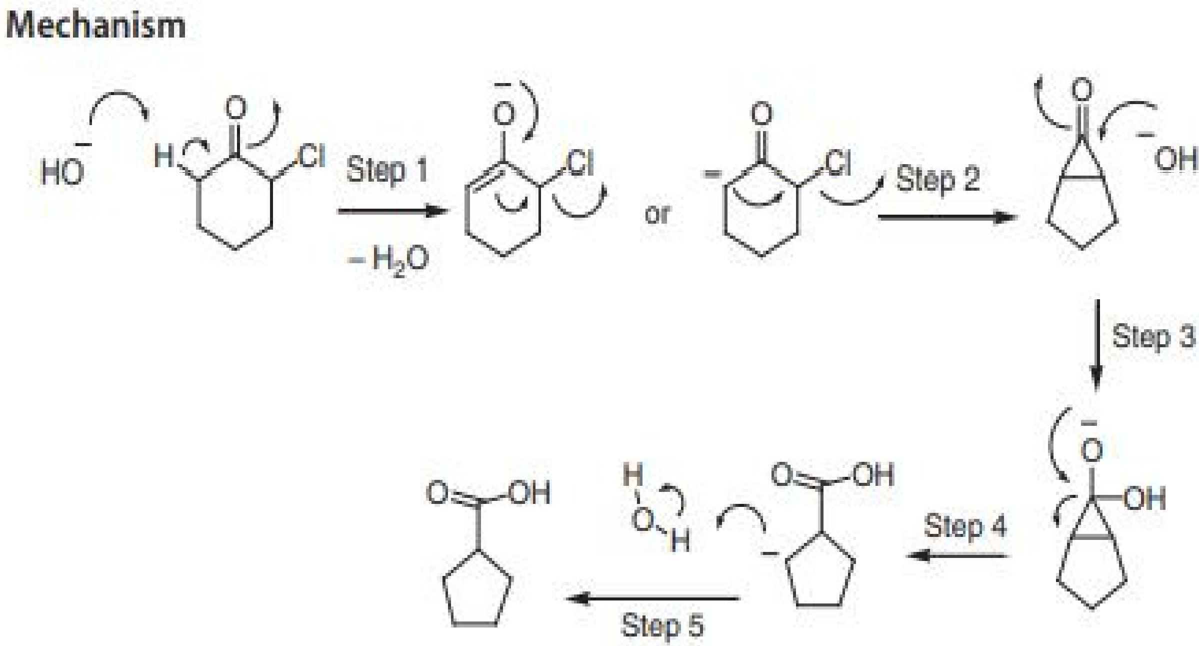



Step 1
Step 2
Step 3
Step 4
Step 5
H2O
Step 3
Step 4
Step 5
H2O

Favorskii Rearrangement

he Favorskii rearrangement is an organic reaction used to convert an α-haloketone to a rearranged acid or ester usir strong base (hydroxide or alkoxide). In case of cyclic α-haloketone, this reaction gives a ring contracted product. The eaction is named after its discoverer the Russian chemist Alexei Yevgrafovich Favorskii.



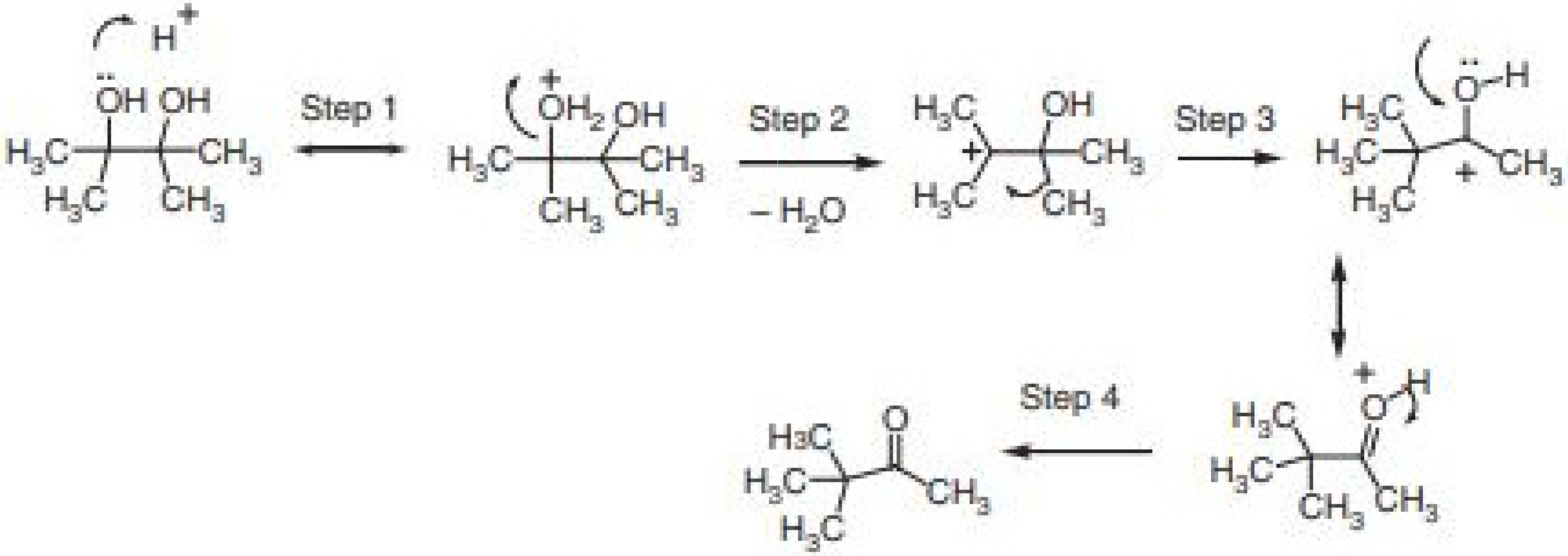

Mechanism

Pinacol–Pinacolone Rearrangement

The pinacol–pinacolone rearrangement is an acid-catalyzed conversion of a 1,2-diol to a carbonyl compound. The name of this reaction comes as pinacol rearranges to pinacolone.

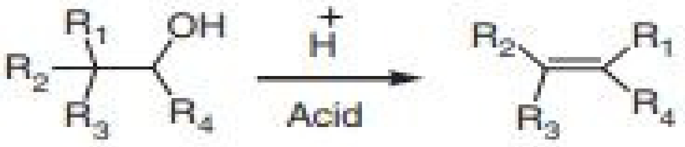
Pinacolone

Pinacol

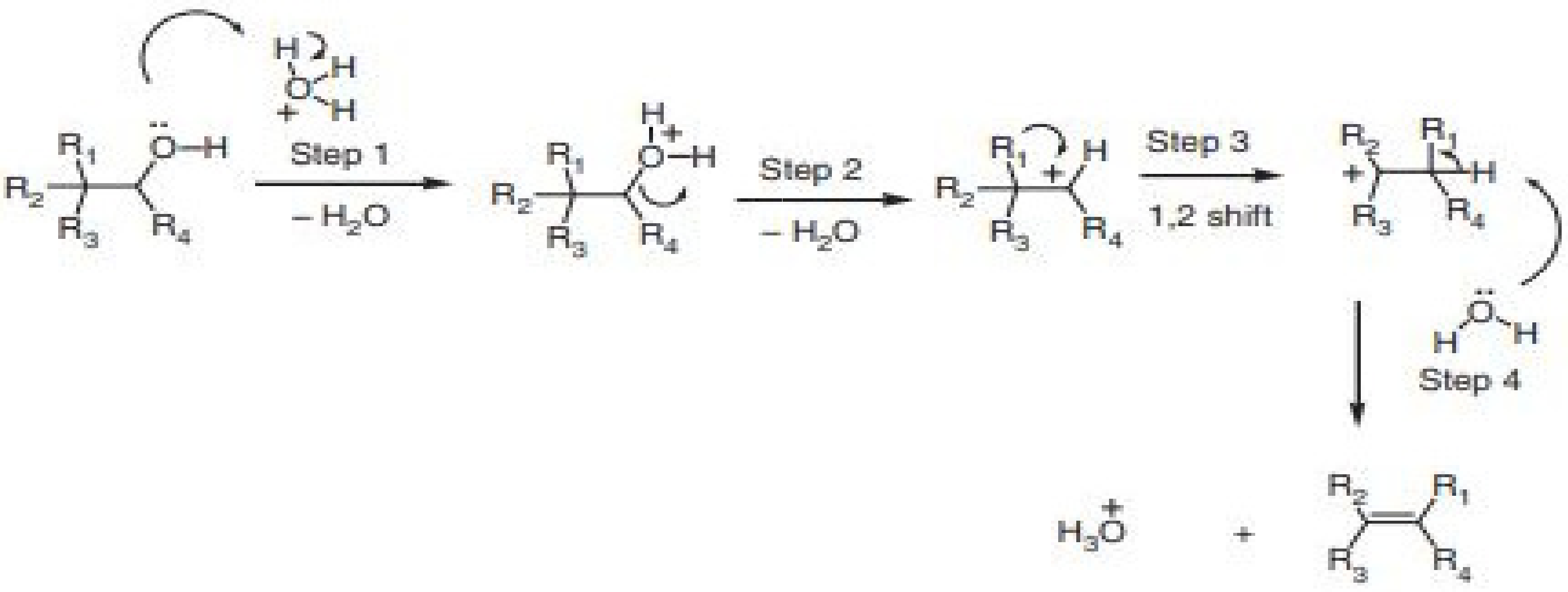


Wagner–Meerwein Rearrangement

e Wagner–Meerwein rearrangement is an acid-catalyzed alkyl group migration of an alcohol to give an olefin with re substituted. This is a cationic [1, 2]-sigmatropic rearrangement reaction. This reaction has been applied to thesize complex natural products and drug molecules.

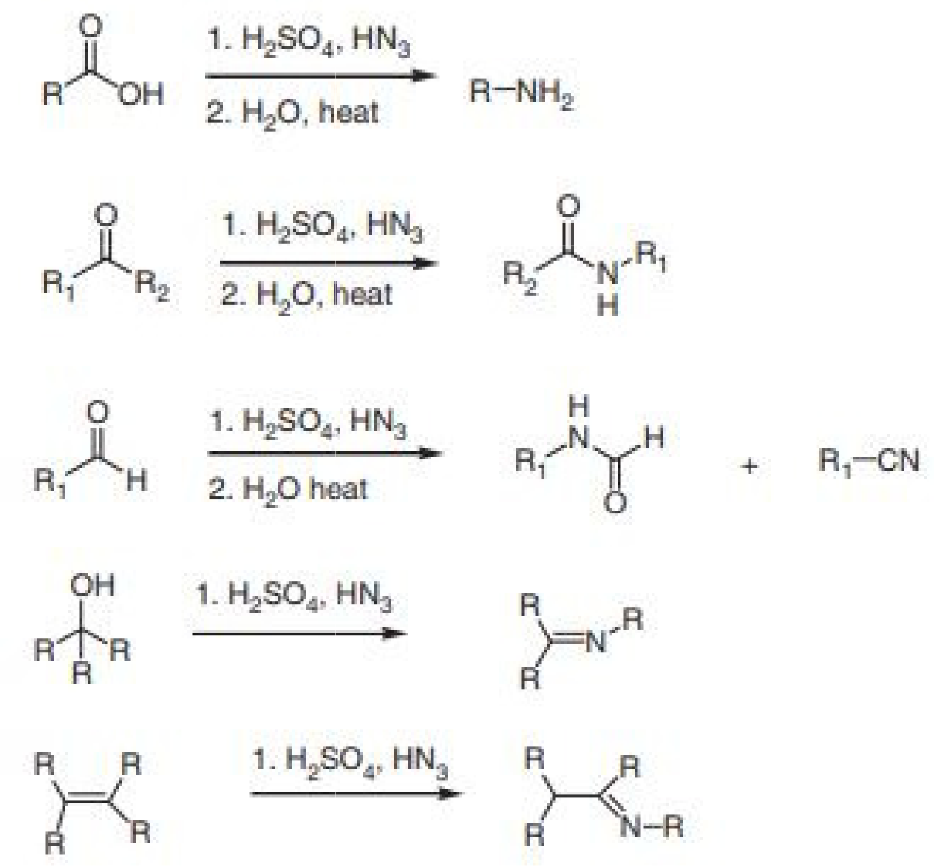


Mechanism

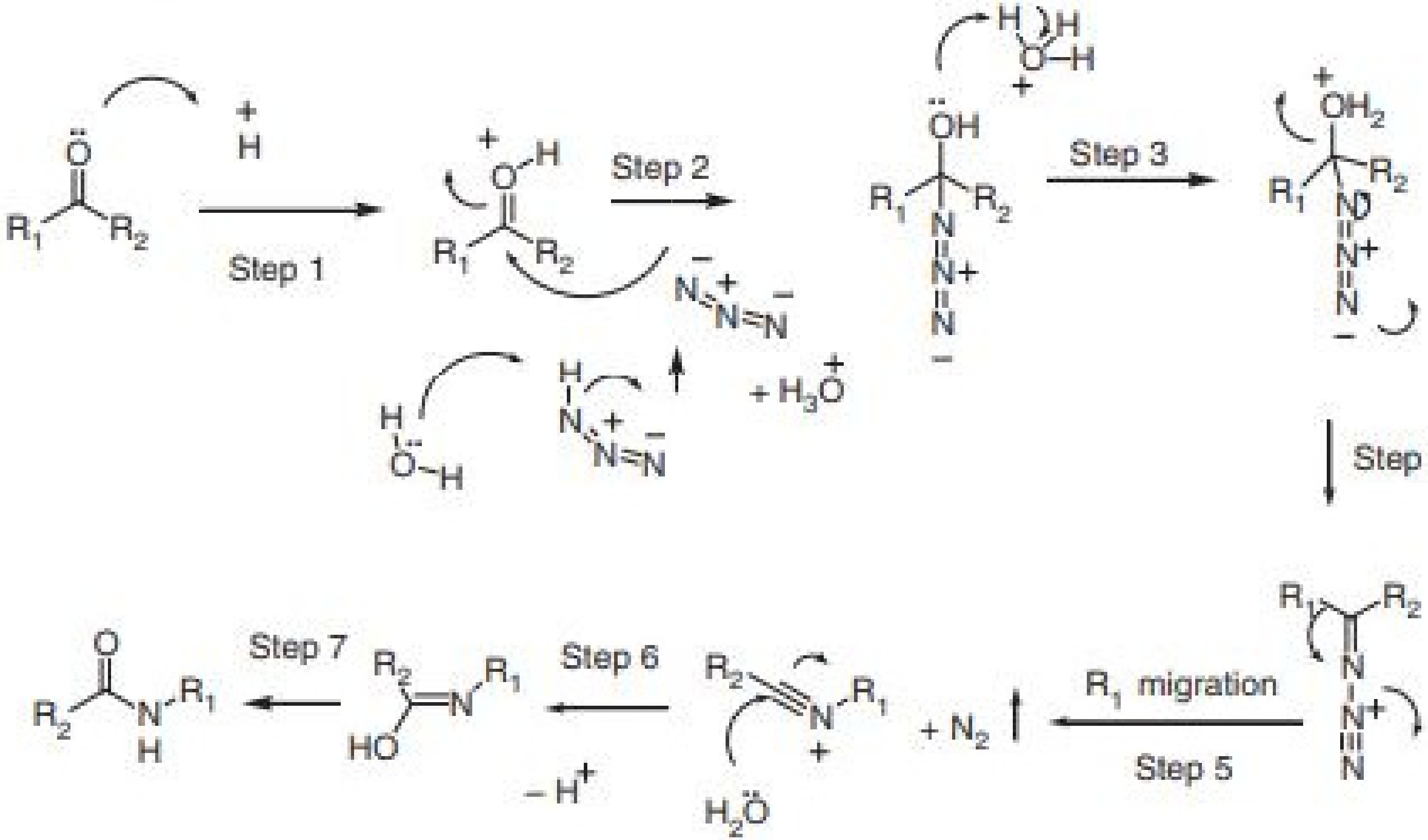


Schmidt Rearrangement or Schmidt Reaction

he Schmidt reaction or rearrangement is an acid-catalyzed reaction of hydrogen azide with a carbonyl compound uch as an aldehyde, a ketone, or a carboxylic acid to give an amine, amide, or nitrile, respectively, after a earrangement and the loss of a molecule of nitrogen gas. This reaction is extended with tertiary alcohol or olefin to ve an imine. The reaction is named after Carl Friedrich Schmidt.



Mechanism



Step 1
Step 2
Step 3
Step 4
R₁ migration
Step 5
Step 6
Step 7
+ H₃O⁺
+ N₂
− H⁺
H₂Ö

THANK YOU