



D.K.M. COLLEGE FOR WOMEN (AUTONOMOUS), VELLORE



eRESOURCES
Digital Learning

E CONTENT TITLE :

- 1. MOLECULAR REARRANGEMENTS (3rd – YEAR)**
- 2. PHENOLS AND NAPTHOLS (II-YEAR)**
- 3. THERMODYNAMICS-(II-YEAR)**

DEPARTMENT : CHEMISTRY

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III-YEAR

ORGANIC CHEMISTRY-II

UNIT- I Molecular rearrangements

1.1 Rearrangements - Classification – Anionotropic, Cationotropic and Free Radical Rearrangements - Intermolecular and Intramolecular Rearrangements – Examples – Cross over experiment – Differences between Intermolecular and Intramolecular rearrangements.

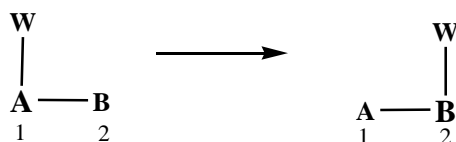
1.2 Mechanisms, Evidences, Migratory Aptitude, Intermolecular or Intramolecular nature of the following rearrangements - Pinacol-Pinacolone, Benzil-Benzilic acid and Beckmann rearrangement.

1.3 Mechanism of Hoffmann, Curtius, Baeyer-Villiger, Claisen (Sigmatropic), Fries rearrangement, Cope and Oxy-Cope rearrangements.

MOLECULAR REARRANGMENT

What are they?

They are reactions in which an atom or a group moves from one atom to another in the same or different molecule, eg.,



where,

A – Migration origin; B-Migration terminus; W- Migrating group/atom.

The migration of an atom or group from one atom to the adjacent atom is called 1,2-shift.

CLASSIFICATION

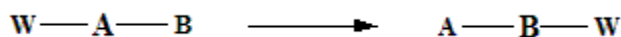
Based on the nature of migrating group or atom rearrangements are classified into three types.

- i. Nucleophilic or Anionotropic rearrangement: migrating group migrates with its electron pair.

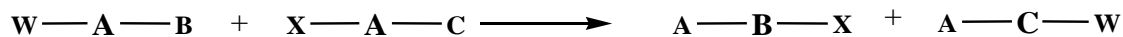
- ii. Electrophilic or Cationotropic rearrangement: migrating group migrates without its electron pair.
- iii. Free radical rearrangement: migrating group migrates with only one electron.

These rearrangements can take place in two possible ways,

- i. **Intramolecular rearrangement:** In this migrating group undergoes migration within the same molecule.



- ii. **Intermolecular rearrangement:** In this migrating group is detached from the migration origin. In this case, migration of group/atom can take place between to different molecule.

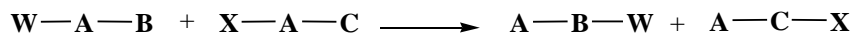


Cross over experiments:

It is an experiment used to predict whether the rearrangement is intramolecular or inter molecular.

This experiment is carried out using a mixture W-A-B and X-A-C, where X is closely related to W and B is related to C. In an intra molecular process only A-B-W and A-C-X are recovered. But if the reaction is inter molecular, then in addition to the above mentioned products A-B-U and A-C-W would also be found.

Intra molecular rearrangement:



Inter molecular rearrangement:

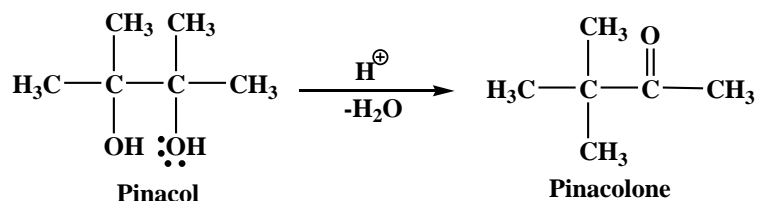


Pinacol-Pinacolone rearrangement:

When vicinal (adjacent) diol also known as pinacol is treated with acids, it rearranges to give aldehyde or ketone. This is called as **Pinacol-Pinacolone rearrangement**. It is an example of 1,2 shift.

The transformation of 1,2-glycol to aldehyde or ketone via rearrangement in presence of strong acid is known as pinacol-pinacolone rearrangement.

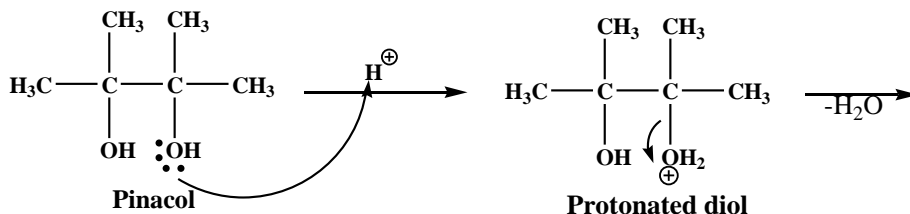
For example, consider the following reaction.

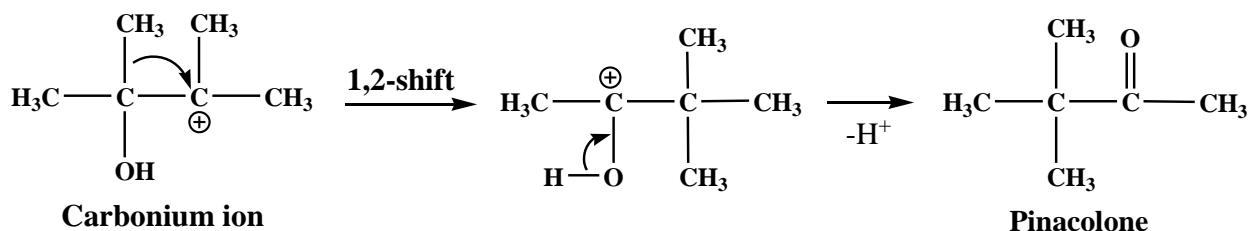


The pinacol-pinacolone rearrangement is general for 1,2-glycol under acid conditions, the migration group may be alkyl or aryl.

Mechanism:

1. A proton is added to one of the hydroxyl group (which can form a stable carbocation)
2. The protonated hydroxyl group is lost as water producing a carbocation
3. The migrating group migrates with a pair of electrons
4. A proton is lost and the product is formed.





In case of unsymmetrical pinacol there are several other points to be considered like which group will be removed, which group will migrate and so on.

Migratory aptitude:

Migratory aptitude is the relative ability of a migrating group to migrate in a rearrangement reactions.

In certain reactions like Beckmann and pinacol rearrangements, if there are more than one choice of group/atom is available in a reaction to migrate, then in such a situations the choice of the migrating group is based on several factor (such as geometry of the molecule). The migratory aptitude groups follow the order of increasing stability of carbocation.

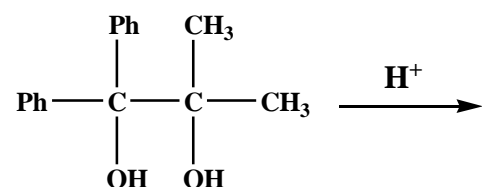
The order of stability of carbocation: $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

In general the migratory aptitude of different groups follows the order,

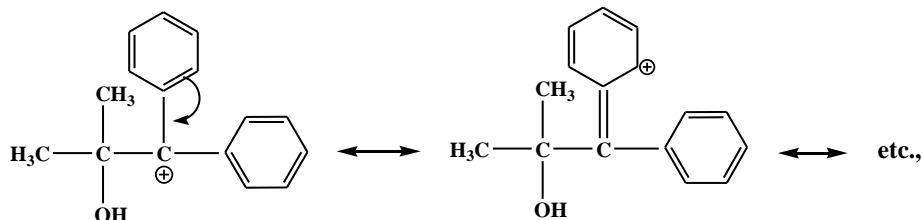


Among the aryl migrating group, **electron-donating substituent** in the para and meta position increase the migratory aptitude, while the same groups in ortho positions decrease them. **Electron-withdrawing groups** decrease migrating ability in all positions.

Predict the product and give the mechanism of the following:

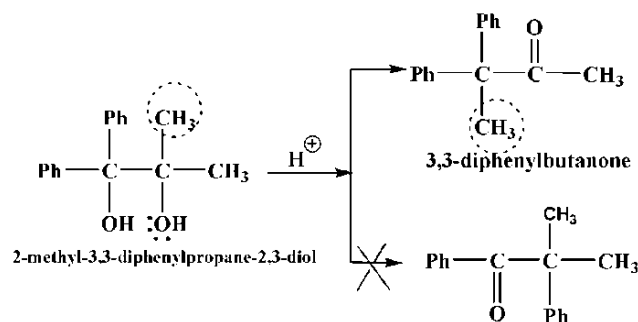


In this example removal of the -OH group present in the carbon attached with two phenyl groups will form a more stable carbocation due to resonance stabilisation as given below.

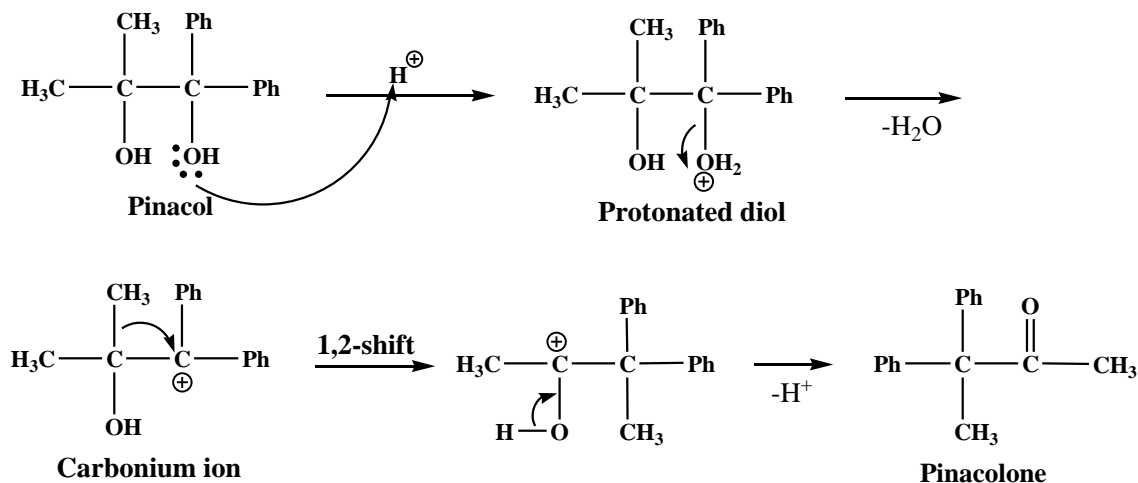


Whereas the carbocation formed by the carbon attached with two methyl groups is stabilized by inductive effect. The stabilization of carbocation due to resonance is greater than inductive effect.

Hence the product is,

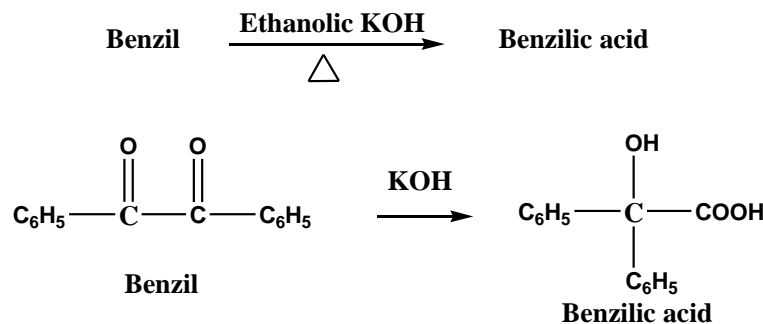


So the mechanism is,

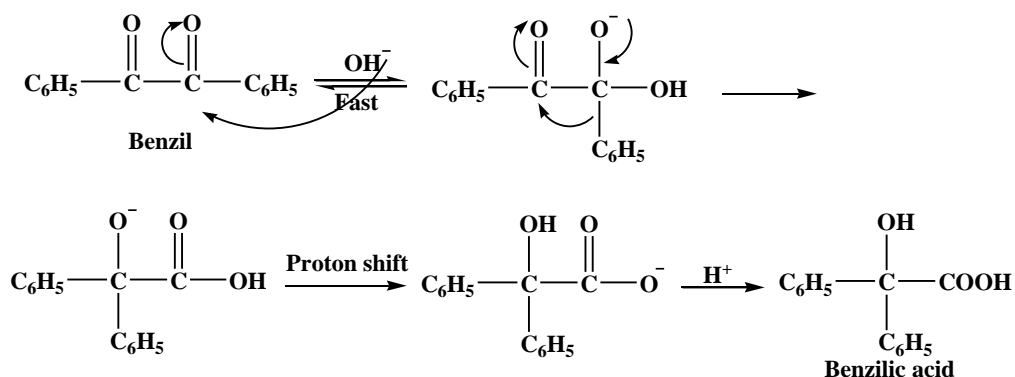


Benzil-Benzilic acid rearrangement:

1,2 Diketones (α -Diketone / benziles) undergo a rearrangement in the presence of strong base to yield α -hydroxycarboxylic acid. This is called as **benzil-benzilic acid rearrangement**. It is an example for 1, 2-shift. This arrangement is applicable for aliphatic diketones also.

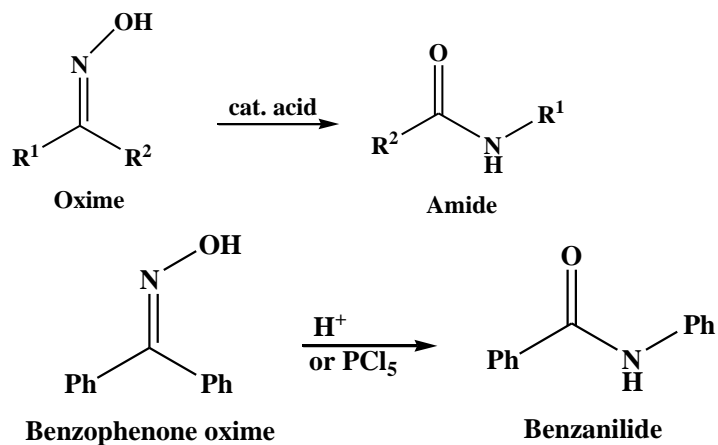
**Mechanism:**

- Reaction is induced by nucleophilic addition of the hydroxide anion to one of the two carbonyl groups of benzil.
- The phenyl group migrates with the bonded electrons to the adjacent carbon atom.
- A proton is transferred to form carboxylic acid

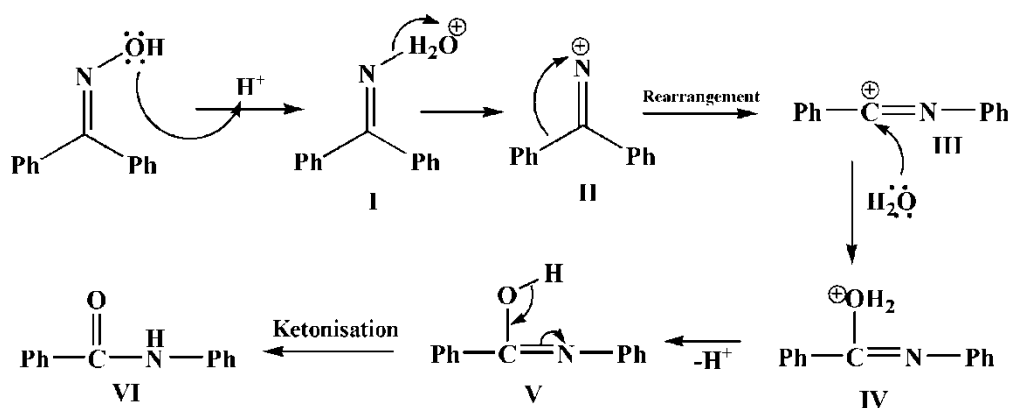
**Beckmann rearrangement:**

The rearrangement of oximes under the influence of a variety of acidic reagents to *N*-substituted amides is known as **Beckmann rearrangement**. Phosphorous pentachloride is commonly used as a catalyst in Beckmann rearrangement, but conc. sulphuric acid, formic acid, thionyl chloride,

polyphosphoric acid etc., can also be used. This is also an example for 1,2-shift.



Mechanism:

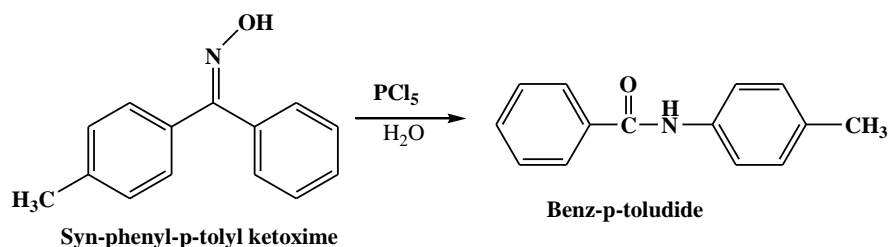


1. A proton is added to hydroxyl group of the oxime to form an intermediate I.
2. The protonated hydroxyl group is lost as water producing an intermediate II.
3. The migrating group migrates resulting in the formation of a carbonium ion III.
4. The carbonium ion adds water yielding the oxonium cation IV.
5. The oxonium cation loses a proton forms an enol derivative of the amide V.

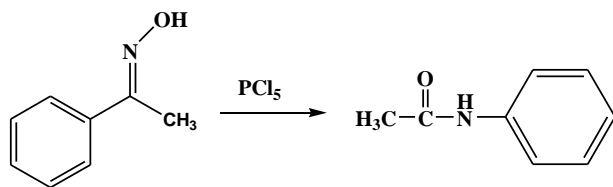
6. The enol V is unstable and ketonises spontaneously giving the final product the amide (VI).

Migratory aptitude:

Beckmann rearrangement leads to different products in case of syn and antiketoxime. The aryl group which is anti to the hydroxyl group of the oxime is one which migrates.

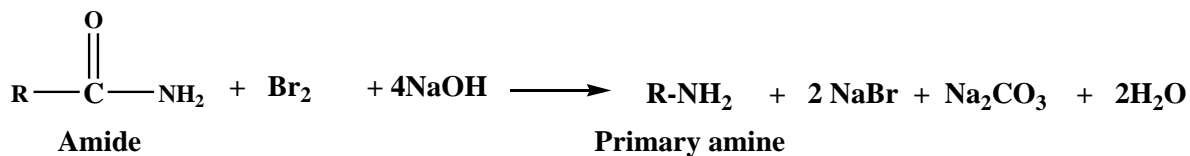
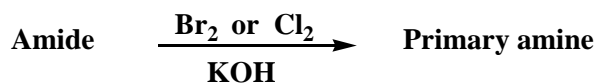


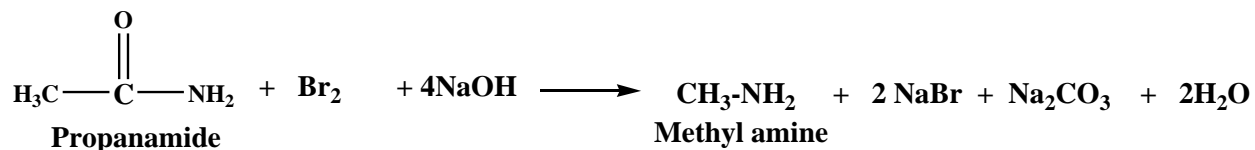
When the oxime is derived from alkyl and aryl ketone it is generally the aryl group which preferentially migrates.



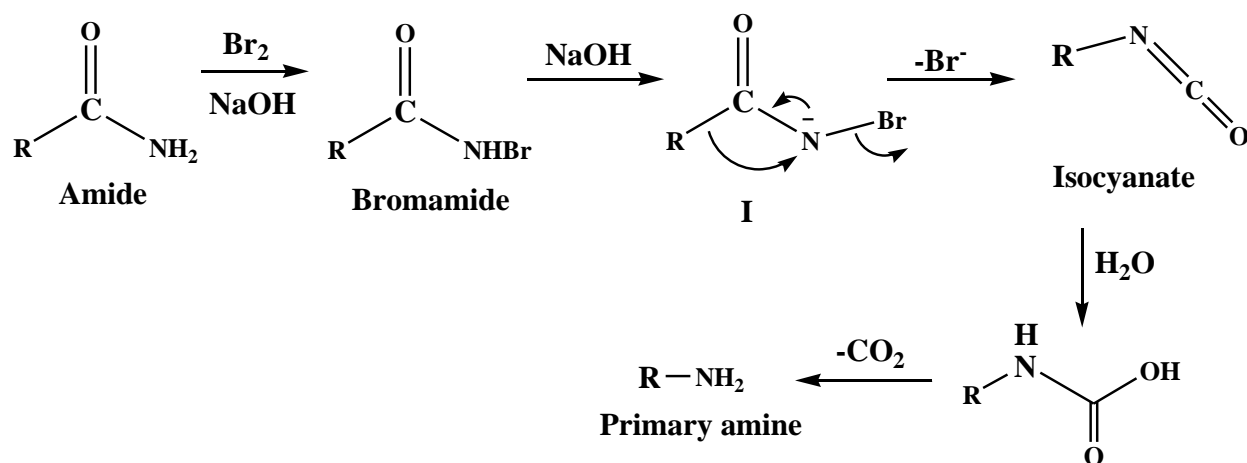
Hofmann rearrangement:

Hoffmann rearrangement also known as Hoffmann degradation. *The reaction of formation of primary amines from amides by shortening of carbon chain with one carbon atom, on treatment with a halogen (chlorine or bromine) in strongly basic (sodium or potassium hydroxide) aqueous medium is known as Hoffmann rearrangement.* It involves migration of R or Ar group.



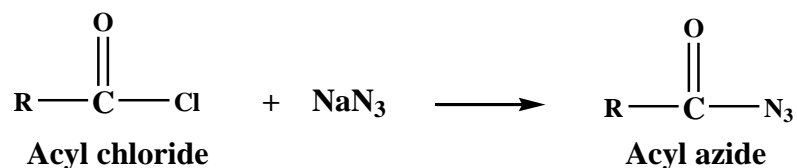
**Mechanism:**

1. The amide is brominated to give the bromamide
2. Since the rearrangement takes place in alkaline media, a proton is eliminated from the bromamide and forms an anion (I)
3. Bromide from (I) is lost so that the nitrogen atom is left with a sextet of electron.
4. Now, the migrating group R migrates from carbon to nitrogen resulting in the formation of isocyanate.
5. The isocyanate is finally hydrolysed to give the amine.

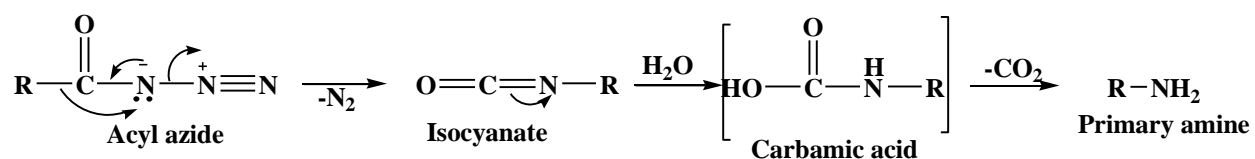
**Curtius rearrangement:**

*The conversion of an acyl azide to an isocyanate under thermal conditions is called as **Curtius rearrangement**.* The mechanism consists of an alkyl shift of the R group from the carbonyl carbon to the electron deficient nitrogen with the release of nitrogen gas.

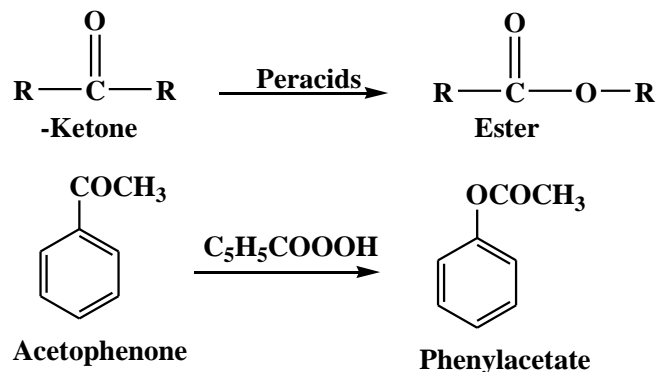
The acid azides required as starting materials may be prepared by action of sodium azide with acyl chloride.

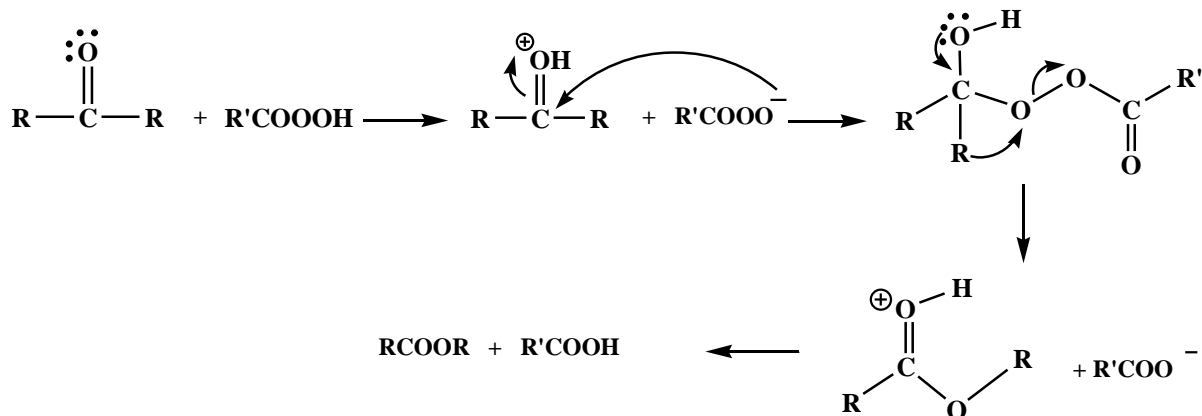
**Mechanism:**

The azide first loses a molecules of nitrogen, with a migration of alkyl group giving isocyanate. The isocyanate then undergoes attack by a variety of nucleophiles such as water, alcohol and amines to yield a primary amine carbonate or urea derivative respectively.

**Baeyer-Villiger rearrangement:**

Ketones on oxidation with peracids or peroxyacids to give an esters is known as **Baeyer-Villiger rearrangement**. This is also known as Baeyer-Villiger oxidation. Caro's acid, perbenzoic acid, *m*-chloroperbenzoic acid (*m*-CPBA) can also be used as oxidizing agents.

**Mechanism:**



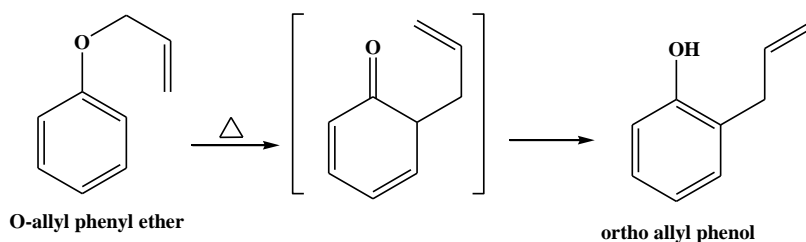
1. Protonation of carbonyloxygen to form a tetrahedral intermediate.
2. Elimination of carboxylate anion and migration of R group to give protonated.
3. Loss of proton to give an ester.

In the tetrahedral intermediate the migratory aptitude of -R group is given below.

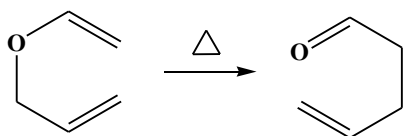
$3^\circ \text{ alkyl} > \text{cyclohexyl} > 2^\circ \text{ alkyl} > \text{benzyl} > \text{phenyl} > 1^\circ \text{ alkyl} > \text{methyl}$

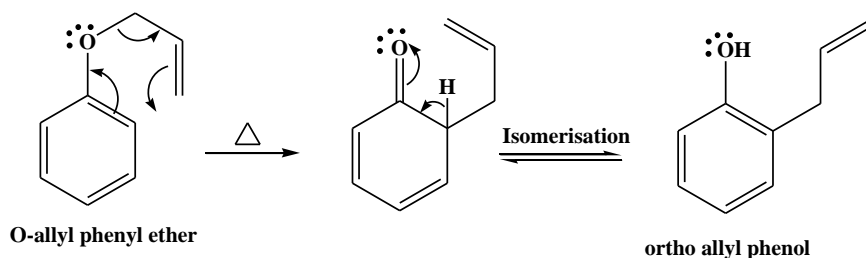
Claisen (Sigmatropic) rearrangement:

When o-allyl ether is heated to about 200°C in the absence of any catalyst, it rearranges to ortho allyl phenol. This thermal rearrangement of phenolic allyl ether is known as Claisen rearrangement.

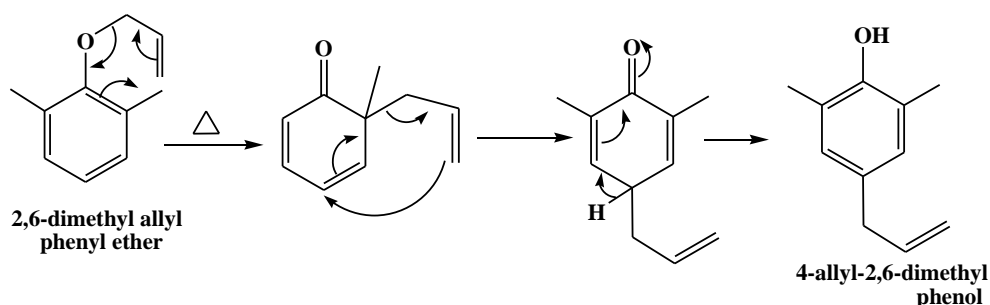


The aliphatic Claisen rearrangement is a [3,3]-sigmatropic rearrangement in which an allyl vinyl ether is converted thermally to an unsaturated carbonyl compound.



Mechanism:

The allyl group migrates almost invariably to the **ortho position unless the ortho positions are blocked**. If both the ortho positions are blocked then the allyl group migrates to para position. This is called **Para-Claisen rearrangement**.



- There is an inversion of the allyl group during the rearrangement occurs. i.e the carbon atom of the allyl group which gets attached to the aromatic nucleus is not the one which is attached to the oxygen atom of the ether. This is confirmed by C¹³ labeling.
- Rearrangement of mixtures of allyl phenyl ethers do not give cross product, suggesting that the rearrangement is truly **intramolecular**.

What is sigmatropic rearrangement?

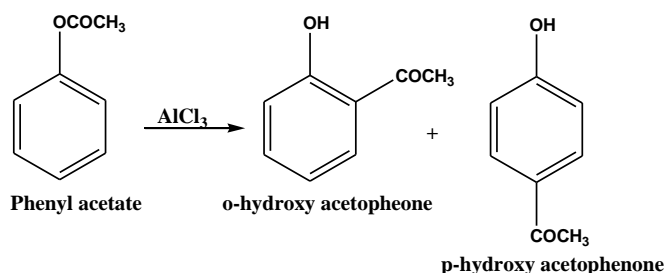
Sigmatropic rearrangement involves shifting of sigma electrons across pi electron conjugated system. In these rearrangements, an atom or a group of atoms shifts from one position to another position. During this rearrangement the total number of σ -bonds and π -bonds remain same both in starting and in final product.

These rearrangements are represented by two numbers in a brackets [i, j], where i, j represents the relative position of the atoms involved in migration.

Claisen and Cope rearrangements are most common examples for sigmatropic rearrangement.

Fries rearrangement:

*The conversion of phenyl esters on heating with aluminum chloride (Lewis acid) to hydroxyl ketones (phenolic ketones) is called **Fries rearrangement**.* The acyl group tends to migrate at ortho or para positions of the aromatic nucleus to give phenolic ketones. Such rearrangements are not possible in alkyl esters.



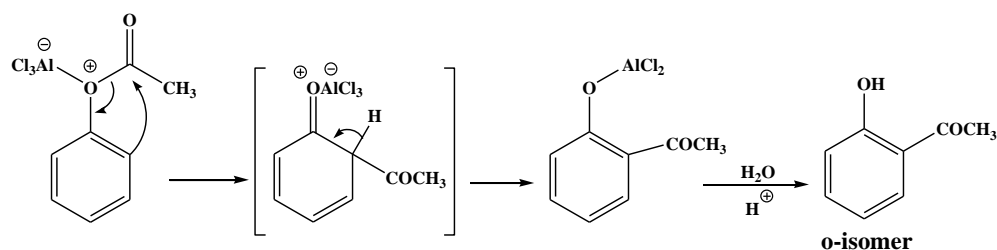
Note:

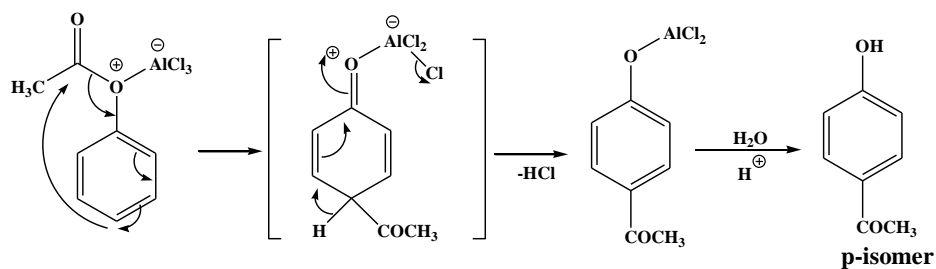
This reaction can be achieved frequently under light and is referred to as the photo Fries rearrangement; this does not need a catalyst and is an intramolecular free radical process.

Mechanism:

The mechanism involves two pathways:

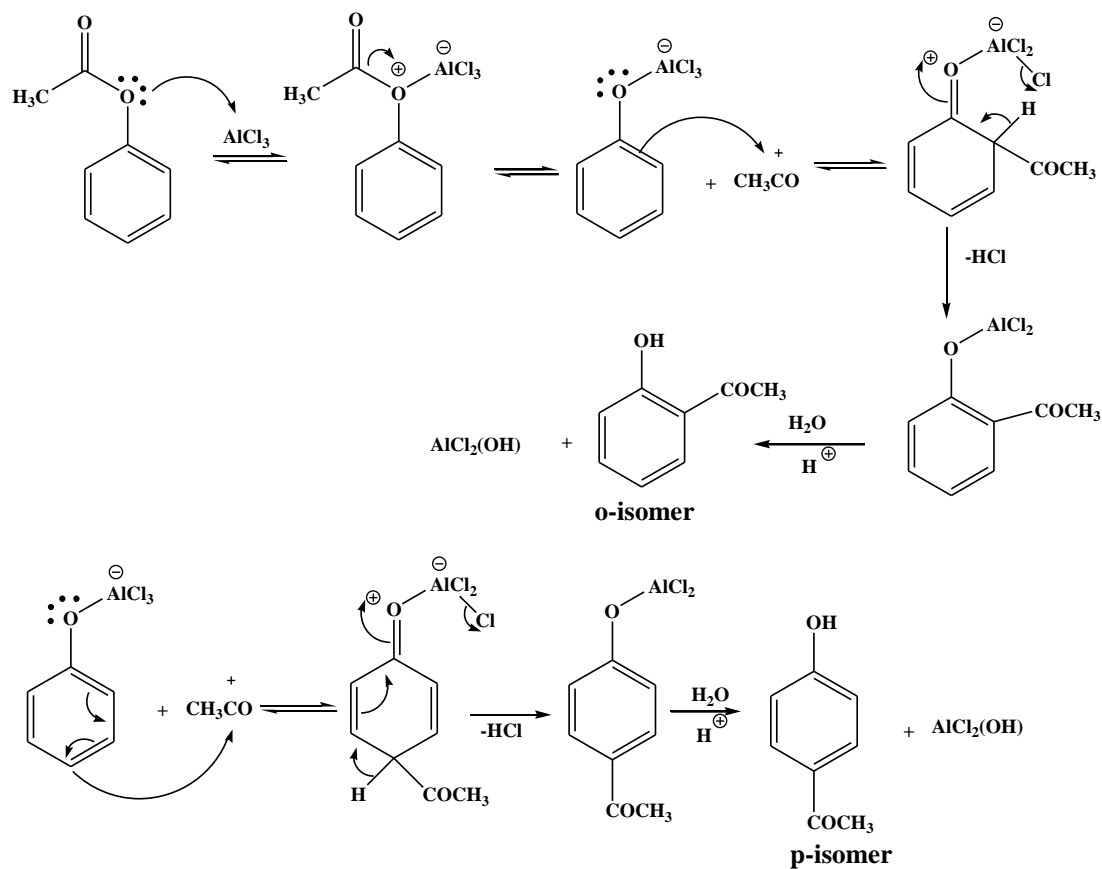
(a) Intramolecular:





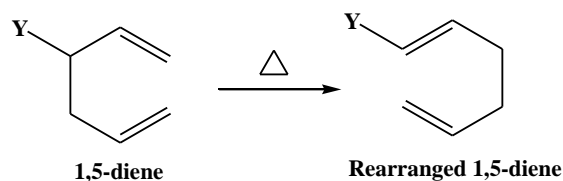
(b) Intermolecular:

It involves the formation of acylium ion followed by Friedel-Crafts acylation at ortho and para position.

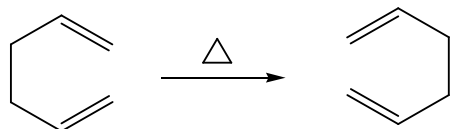


Cope rearrangement:

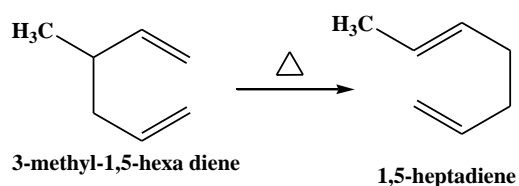
The thermal isomerization of a 1,5-dienes by a 3,3-sigmatropic shift is known as **Cope rearrangement**.



The unsubstituted 1,5-dienes also undergo this rearrangement. Since the product is identical with the reactant it is impossible to prove that the rearrangement has taken place.



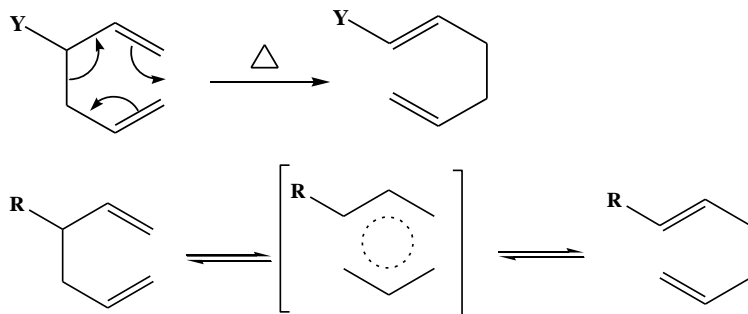
On the other hand, if substituted dienes with an unsymmetrical carbon either is position 3 or 4 is heated, the product clearly shows that the compound has undergone Cope rearrangement.

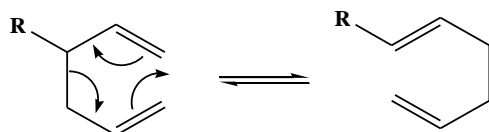


Mechanism:

It has been shown that this rearrangement proceeds through six centered 'pericyclic process'.

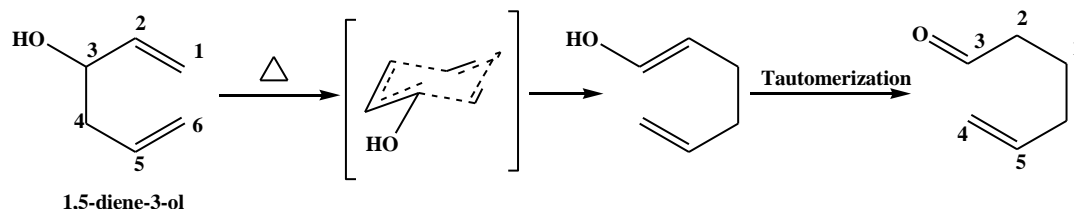
Note: The reactions which proceed in a single step via the formation of a cyclic transition intermediate involving the migration of π and σ -electrons are called pericyclic reactions.-



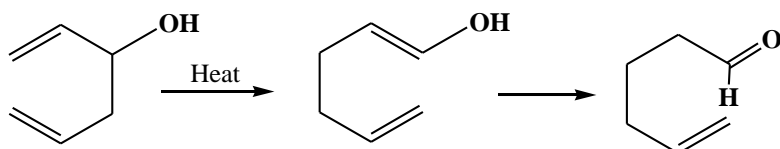


Oxy-Cope rearrangement:

The oxy-Cope rearrangement is a variation of the Cope rearrangement in which 1,5- diene-3-ols are converted to unsaturated carbonyl compounds by a mechanism typical for such a [3,3]-sigmatropic rearrangement.



In the oxy-Cope rearrangement a hydroxyl group is added at C3 forming an enal or enone after keto-enol tautomerism of the intermediate enol.



Reference Books:

1. Text Book of Organic Chemistry – P.L.Soni – Sultan Chand (1994).
2. Advanced Organic Chemistry – Bahl and Arun Bahl – S. Chand (1987).
3. A text book of Organic Chemistry - K.S.Tewari, N.K.Vishal, S.N.Mehrotra - Vikas Publishing House (2006).
4. Organic reaction mechanisms – Gurdeep Chatwal- Himalaya Publishing House (2008).
5. Organic reaction mechanisms – V.K. Ahuwalia , Rakesh Kumar Parashar – Narosha Publising House (2009).

II-YEAR

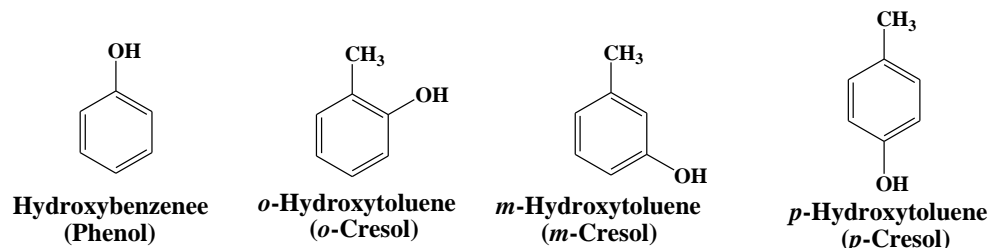
GENERAL CHEMISTRY-IVUNIT-III

3.2 Phenols - Acidic character of phenols - Kolbe's reaction, Reimer-Tiemann reaction, Gattermann , Lederer-Manasse, Houben-Hoesh, Friedel-Crafts, Schotten-Baumann and Liebermann's Nitroso Reaction.

3.3 Preparations, Properties and Uses of alpha and beta Naphthols

Phenols are the hydroxyl derivatives of aromatic hydrocarbons and contain one or more –OH group directly attached to the aromatic ring.

Eg.,

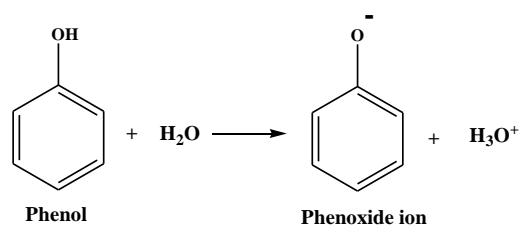
**Properties:**

- Pure phenols are colourless liquids or crystalline solids. They turn pink/red on exposure to air and light due to oxidation.
- They have antiseptic properties
- They are weakly acidic in nature. They turns aqueous blue litmus to red.

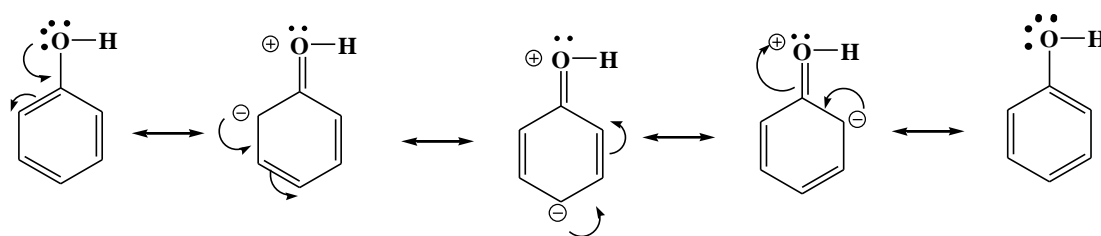
Acidic character of phenols:

Phenols are fairly acidic in nature and react with alkali metals and sodium and potassium hydroxide to form salts known as **phenoxides**. However phenols are not sufficiently acidic to react with sodium bicarbonate or carbonate. Phenols are weaker acids than carbonic acids.

Reason for acidic nature of phenols: (Explanation on the basis of resonance and stabilization).

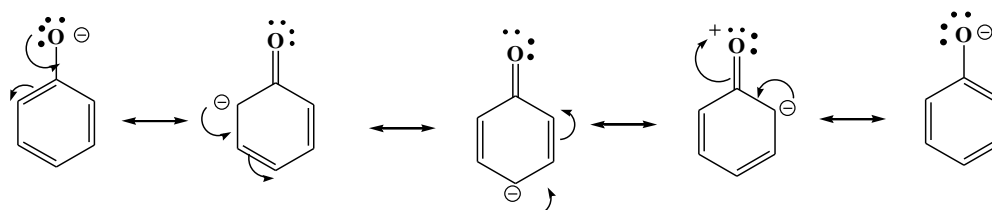


1. Due to resonance the oxygen atom of the –OH group acquires a positive charge which help in the release of a proton.



Resonance structures of phenol

2. In the dissociation of phenol to phenoxide ion and a proton the equilibrium lies mainly towards the right hand side as the resulting phenoxide ion is more stabilized by resonance as compared to phenol.



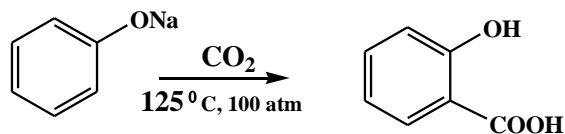
Resonance structures of phenoxide ion

Since the contributing structures of phenol are dipolar structures having both +ve and –ve charges in the molecules, their stability is low. In case of phenoxide ion since only a negative resonance is comparatively high. *Hence phenoxide ion is resonance stabilized to a greater extent as compared to phenol.*

Kolbe's reaction / Kolbe–Schmitt reaction :

When sodium phenoxide is heated with carbon dioxide under high pressure, a carboxylic group is introduced in o- position to the –OH group.

Small amount of *p*- isomer is also obtained in this reaction. If the reaction is carried out at higher temperature.

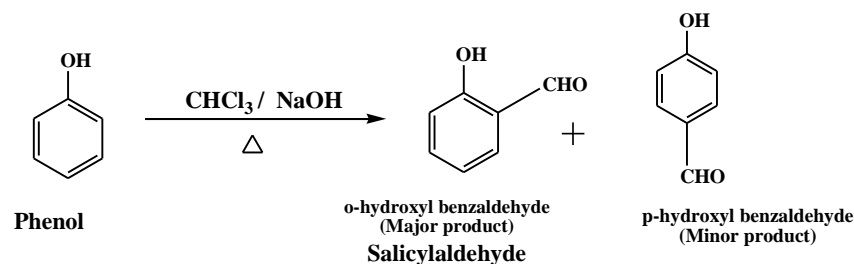


Sodium Phenoxide

Salicylic acid

Reimer- Tiemann reaction (formylation):

When phenol is refluxed with chloroform in the presence of sodium hydroxide an aldehyde group is formed at ortho position of the –OH group. Small amount of *p* - product is also obtained. This formylation reaction is known as Reimer-Tiemann reaction.

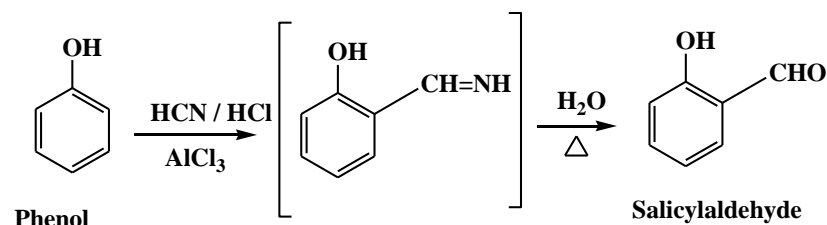


Phenol

o-hydroxyl benzaldehyde
(Major product)
Salicylaldehydep-hydroxyl benzaldehyde
(Minor product)

Gattermann reaction: (formylation)

When phenol is treated with a mixture of hydrogen cyanide and HCl in the presence of aluminum chloride catalyst an aldehyde is introduced in the ortho position. For example,

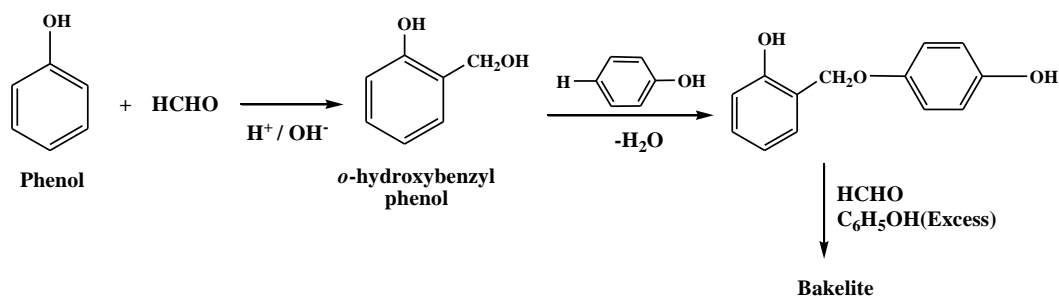


Phenol

Salicylaldehyde

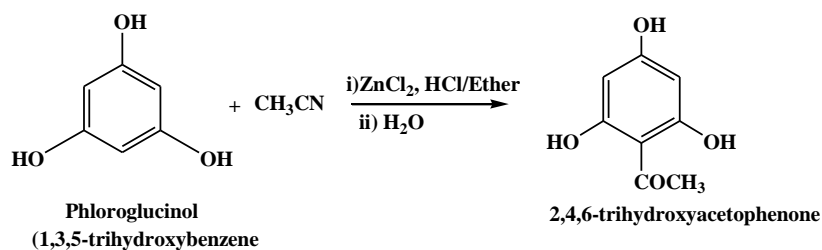
Lederer – Manasse reaction:

Formaldehyde condenses with phenol in alkaline or acidic medium to form *o*-hydroxybenzylalcohol which further condenses with phenol to give polymer, **Bakelite**. This is called **Lederer-Manasse reaction**.



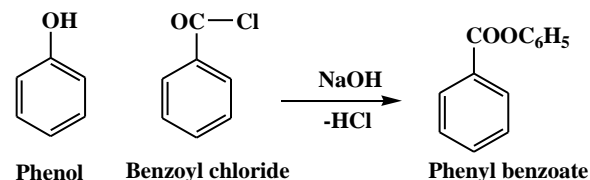
Houben- Hoesh reaction(acylation):
(specific reaction of polyhydric phenols)

Polyhydric phenols when treated with alkyl cyanide and dry HCl in the presence of anhydrous $ZnCl_2$, in ether solution gives a **ketimine hydrochloride**, which on hydrolysis with steam gives an acyl derivative of polyhydroxy phenol. **Phenol does not** give this reaction.



Schotten- Baumann reaction:

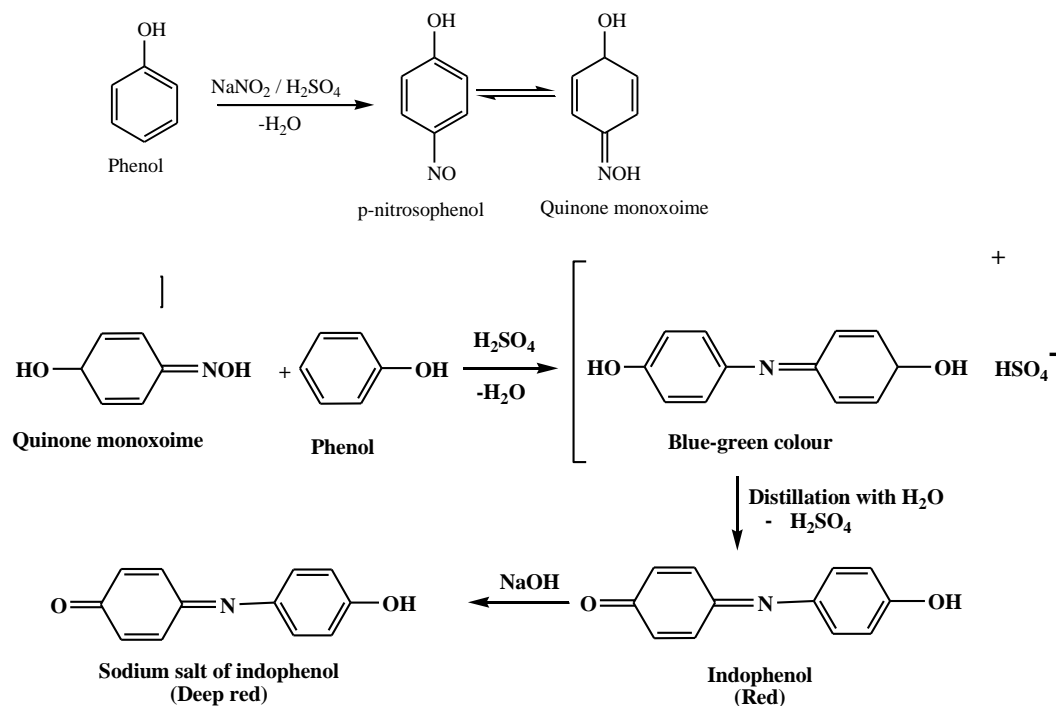
The Process of **benzoylation** of compounds containing active hydrogen such as phenol, Aniline, Alcohol etc. with benzoyl chloride in the presence of aqueous NaOH is called **Schotten Baumann** reaction.



Liebermann's Nitroso Reaction:

When phenol is warmed with a mixture of sodium nitrite and conc. H_2SO_4 then blue/green colour is obtained. This reaction mixture when diluted with water, the colour becomes red but again turns deep blue on addition of

excess of NaOH solution. This is called as *Liebermann's nitroso reaction*. This test is also known as *Liebermann's test*. It is an important test to distinguish phenols from alcohols.



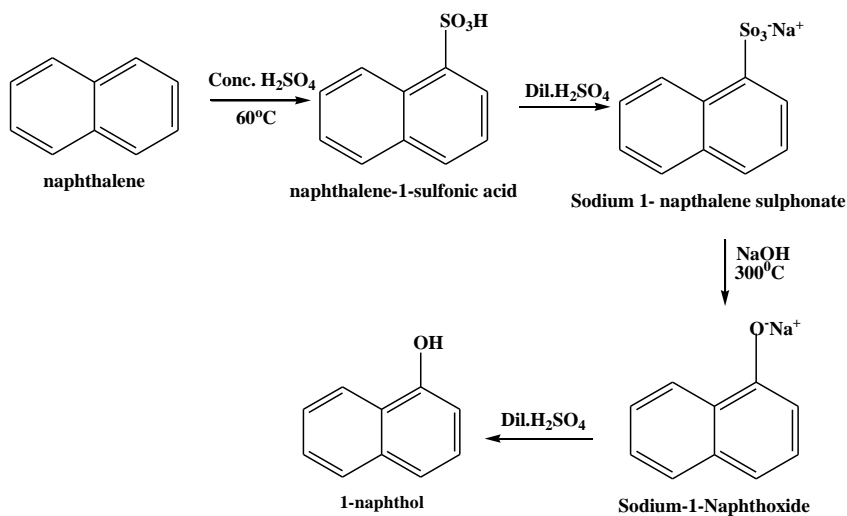
Naphthols

- The hydroxyl derivatives of naphthalene are known as naphthols.
- It has molecular formula $\text{C}_{10}\text{H}_7\text{OH}$.
- It can exist as two isomeric forms i.e., α -naphthol and β -naphthol.
- These can be differentiated by the connectivity of hydroxyl group in to naphthalene ring.

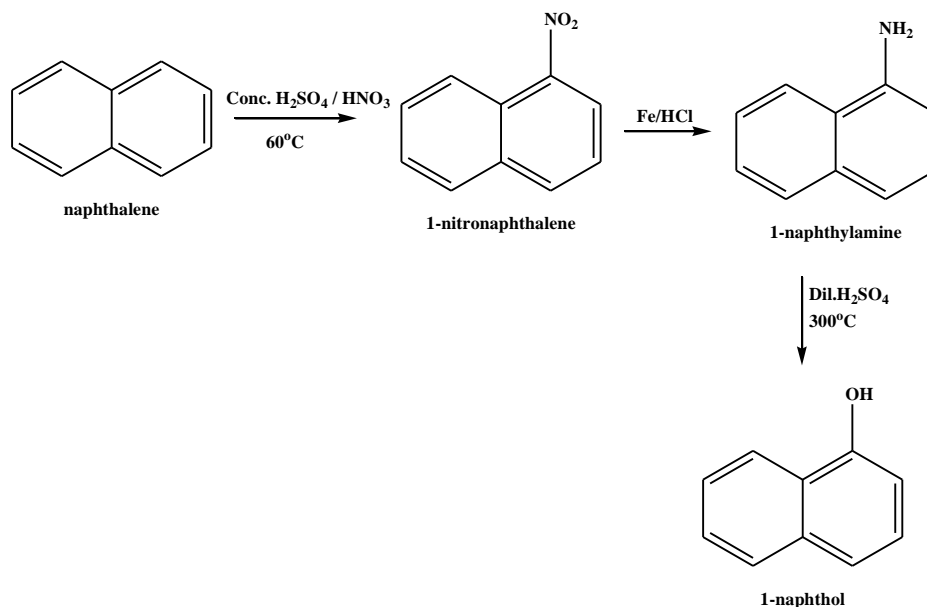
α -naphthol/ 1-naphthol**Preparation:**

α -naphthol can be prepared from naphthalene by two methods as given below.

- a) Naphthalene on treatment with conc. H_2SO_4 at 60°C gives α -naphthalene sulphonicacid which on treatment with NaOH gives sodium 1-naphthalenesulphonate. When sodium 1-naphthalenesulphonate is fused with sodium hydroxide at 300°C , it gives sodium 1-naphthoxide. Treatment of this with dilute sulphuric acid yields 1-naphthol or α -naphthol.



- b) Naphthalene is treated with a nitrating mixture i.e., Con. H_2SO_4 and Con. HNO_3 at 60°C gives α -nitronaphthalene which on reduction with Fe and HCl give 1-naphthylamine. 1-naphthylamine when heated with dilute sulphuric acid at 300°C under pressure gives 1-naphthol.



Properties

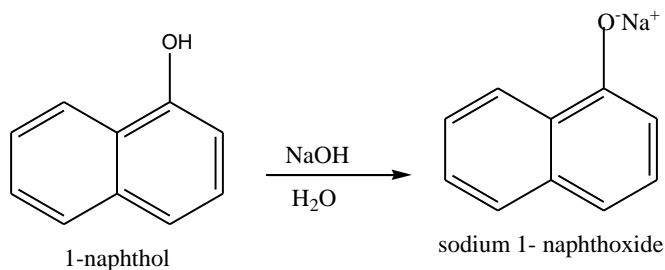
Physical Properties

- It is a colourless crystalline solid, melting point is 94°C .
- Insoluble in water but soluble in alcohol and ether.
- It has faint phenolic odour and resembles phenol in its chemical properties.
- It is an aromatic compound.
- It is a highly polar molecule.

Chemical Properties

a) Acidic Character

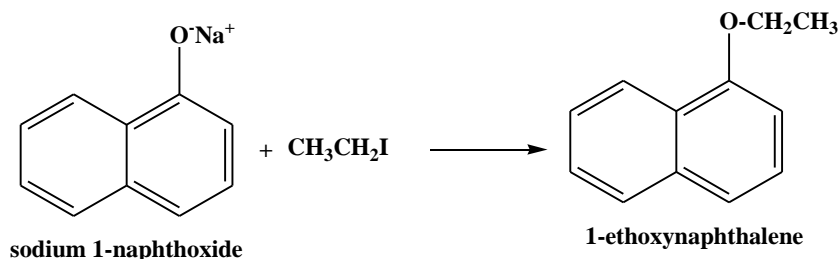
1-naphthol is a weak acid. It dissolves in sodium hydroxide or sodium carbonate and forms water soluble sodium 1-naphthoxide.



1-naphthol ionizes in water to yield a resonance stabilized naphthoxide ion so it has weak acidic character but it is a stronger acid than phenol. The increased acidity is due to the greater stability of the naphthoxide ion as compared to the phenoxide ion. In the naphthoxide ion negative charge is delocalized over two aromatic rings whereas in the phenoxide ion it is delocalized over the ring.

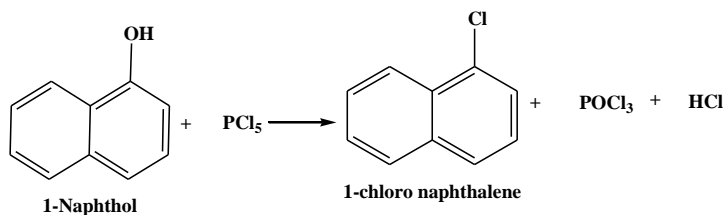
b) **Williamson's Synthesis** (reaction with alkyl halides)

When sodium 1-naphthoxide is heated with alkyl halides, the corresponding ethers are formed.



c) **Reaction with Phosphorous Pentachloride**

1-naphthol reacts with PCl₅ to form 1-chloronaphthalene.

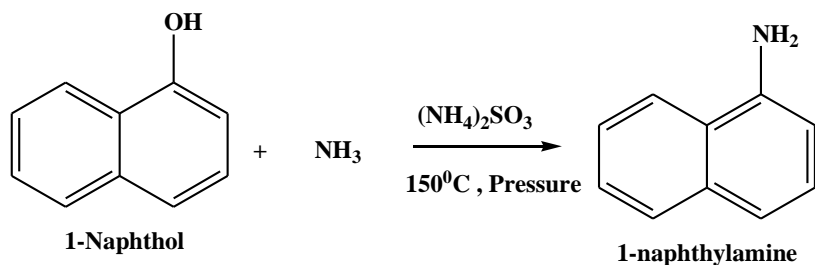


d) **Bucherer Reaction**

The reversible conversion of a α -naphthol into the corresponding naphthylamine is called the Bucherer Reaction. α -naphthol reacts with

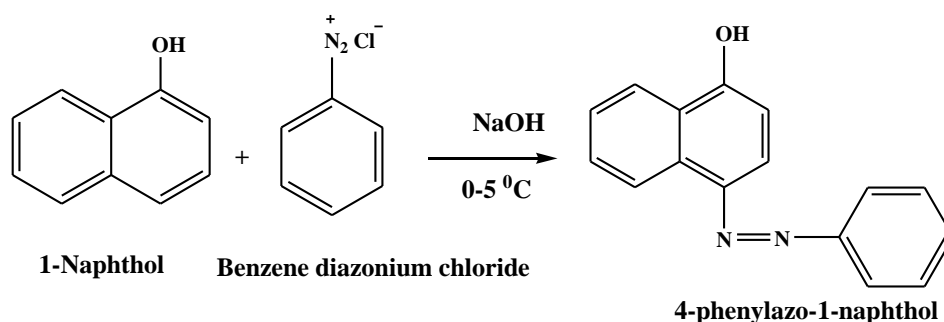
ammonia and ammonium sulphite at
yield 1-naphthylamine.

150 °C under pressure to



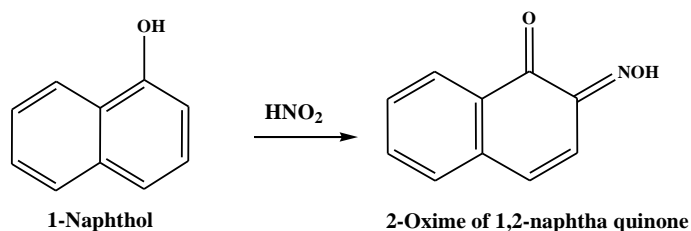
e) Azo - coupling

α -naphthol reacts with benzenediazonium chloride in a weakly alkaline solution at 0-5 °C to give 4-phenylazo-1-naphthol.



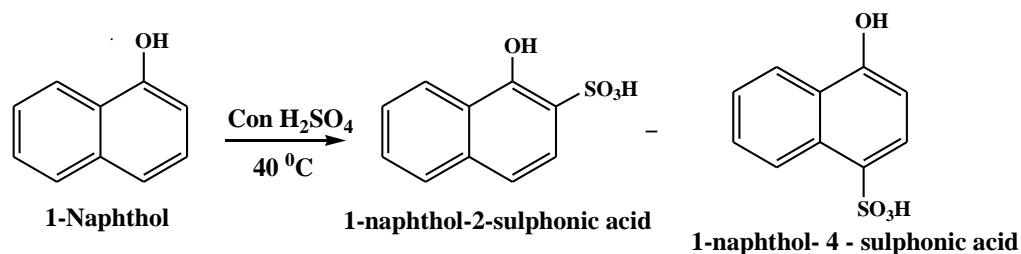
f) Reaction with nitrous Acid

α -naphthol reacts with nitrous acid to give 2-oxime of 1,2-naphthaquinone



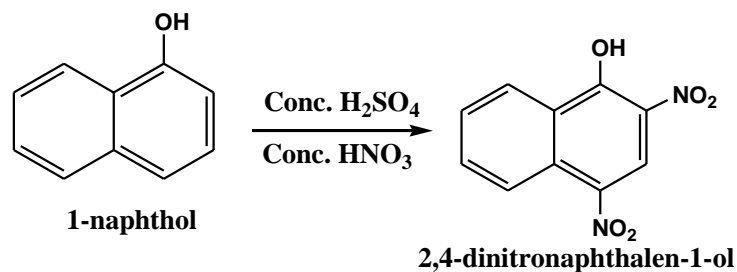
g) Sulphonation

α -naphthol reacts with concentrated sulphuric acid at 40°C to yield a mixture of 1-naphthol-2-sulphonic acid and 1-naphthol-4-sulphonic acid. These sulphonic acids are used in manufactures of azo dyes.



h) Nitration

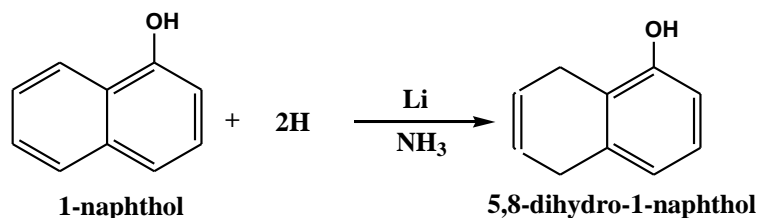
α -naphthol reacts with nitrating mixture at 20°C to give 2,4-dinitronaphthol



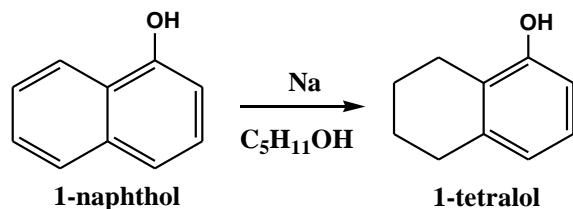
i) Reduction

Brich Reduction

(i) α -naphthol reacts with lithium metal in liquid ammonia to yield 5,8-dihydro-1-naphthol.

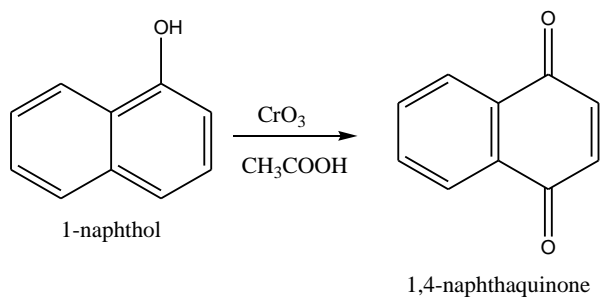


(ii) α -naphthol reacts with sodium metal in isopentanol and gives α -tetralol

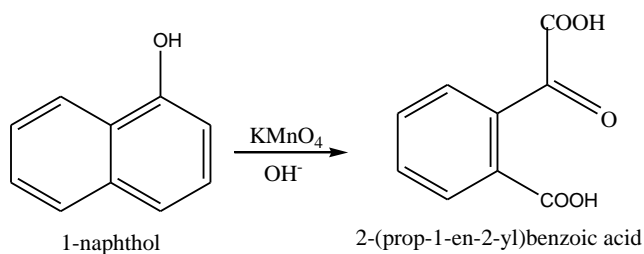


j) Oxidation

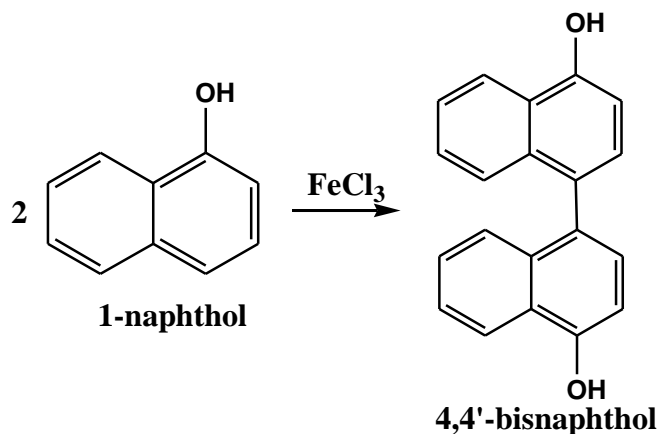
- (i) α -naphthol is oxidized by chromium trioxide in acetic acid to give 1,4-naphthaquinone



- (ii) α -naphthol is oxidized by alkaline potassium permanganate to phthalonic acid.



- (iii) Oxidation of α -naphthol with ferric chloride yields a blue violet precipitate of 4,4'-bis-1-naphthol or α -binaphthol

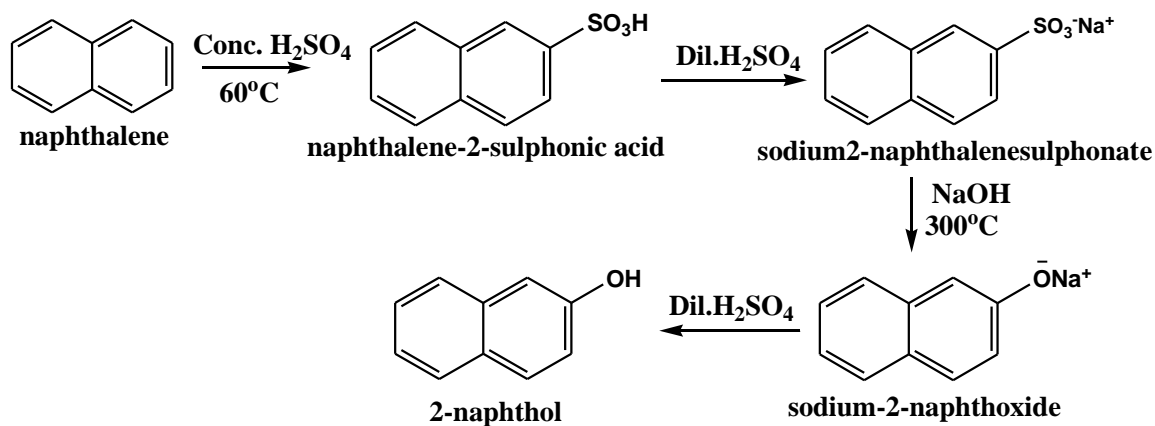


Uses

- α -naphthol is used in the manufacture of insecticides.
- It is used in the Molisch test to identify carbohydrates.
- α -naphthol and their derivatives are used in dyes.

β -naphthols / 2- naphthols**Preparation:**

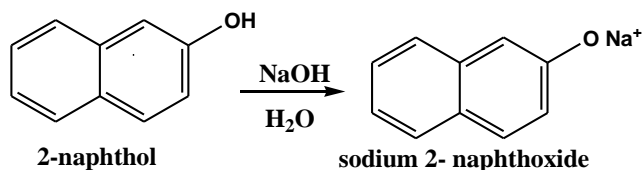
β -naphthols can be prepared from naphthalene, it is treated with $\text{Con. H}_2\text{SO}_4$ at 165°C gives 2-naphthalene sulphonic acid which on treatment with NaOH gives sodium 2-naphthalenesulphonate. When sodium 2-naphthalenesulphonate is fused with sodium hydroxide at 300°C , it gives sodium 2- naphthoxide. Treatment of this with dilute sulphuric acid yields 2-naphthol or β -naphthol.

**Properties:****Physical properties**

- It is a colourless solid
- Melting point is 123°C
- It is slightly soluble in water and completely soluble in ether and ethanol

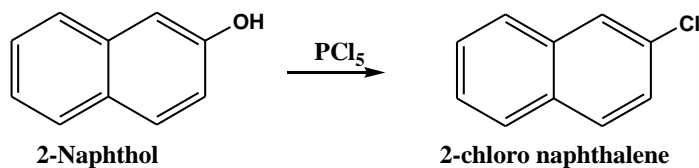
Chemical properties**a) Acidic character**

β -naphthol is a stronger acid than phenol. It dissolves in sodium hydroxide or sodium carbonate solution to give water soluble 2-naphthoxide.



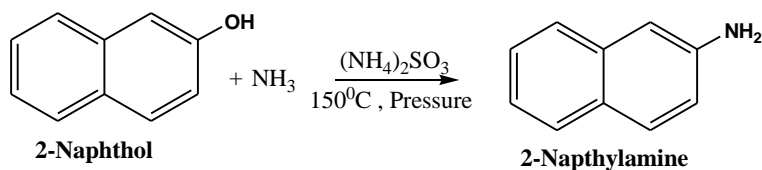
b) Reaction with phosphorous pentachloride

β -naphthol reacts with PCl_5 to give 2-chloronaphthalene.



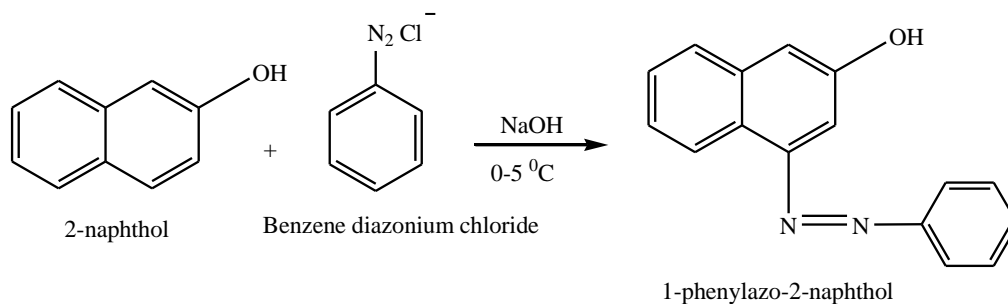
c) Bucherer Reaction

β -naphthol reacts with ammonia and ammonium sulphite at 150°C under pressure to yield 2-naphthylamine.



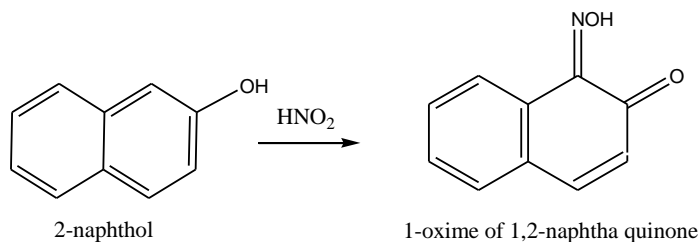
d) Azo coupling

β -naphthol reacts with benzenediazonium chloride in a weakly alkaline solution at $0-5^\circ\text{C}$ to form 1-phenylazo-2-naphthol



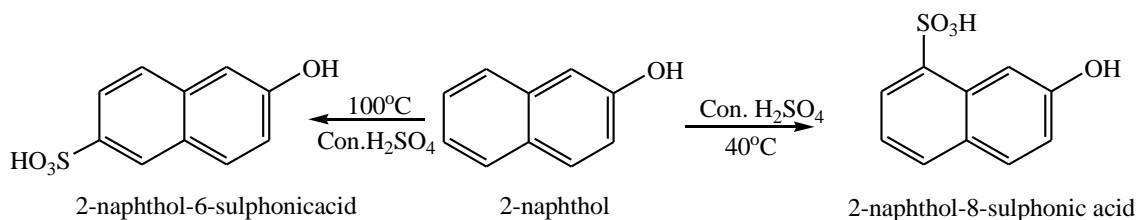
e) Reaction with Nitrous acid

β -naphthol reacts with nitrous acid to give 1-oxime of 1,2-naphthaquinone.



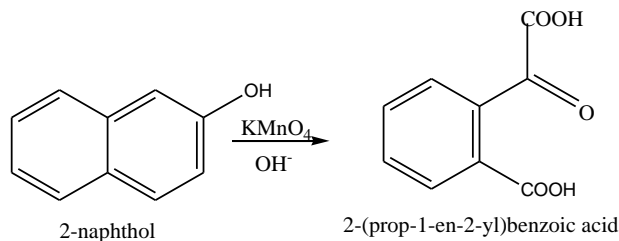
f) Sulphonation

β -naphthol reacts with concentrated sulphuric acid at 40°C to yield 2-naphthol-8-sulphonic acid. When this reaction is carried at 100°C it undergoes rearrangement to give 2-naphthol-6-sulphonic acid.

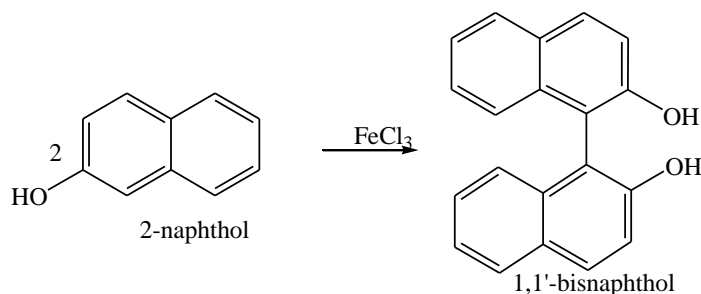


g) Oxidation

(i) β -naphthol reacts with alkaline potassium permanganate to phthalonic acid.

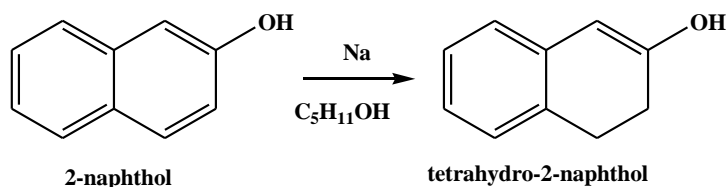


(ii) Oxidation of β -naphthol with ferric chloride yields a green precipitate of 1,1'-bis 2-naphthol or β -dinaphthol



f) Reduction

β -naphthol reacts with sodium metal in isopentanol and gives tetralol or tetrahydro-2-naphthol



Uses

- β -naphthol is used in the manufacture of dyes.
- It is used as an antioxidant in the manufacture of synthetic rubber.
- It is used as an antiseptic in the treatment of the skin diseases.
- It is used to prepare methyl and ethyl esters which are extensively used in perfumery.

UNIT-IV

4.1 Free energy and Work function - Gibbs free energy – Helmholtz free energy – Relationship between Gibbs free energy and Helmholtz free energy – Their variations with Temperature, Pressure and Volume – Free energy change as criteria for Equilibrium and Spontaneity.

4.2 Maxwell's Relations – Thermodynamic Equation of State.

4.3 Gibbs-Helmholtz equation - Derivation and Applications - Clausius-Clapeyron equation - Derivation and Applications.

Helmholtz free energy (Work function) (A) :

The work function (A) is defined as

$$A = E - TS$$

where E is the internal energy of the system, T its absolute temperature and S is entropy. Since E, T and S depend upon the thermodynamic state of the system only, it is evident that the function A is also a state function.

Let the values of the three functions in the above equation in a given state of the system at constant temperature T, be A₁, E₁ and S₁, so that

$$A_1 = E_1 - T S_1 \dots\dots\dots(1)$$

Let an appreciable changes take place at the same temperature T so that the values of the three functions in another state of the system A2, E2 and S2.

Then,

$$A_2 = E_2 - T S_2 \dots\dots\dots(2)$$

Subtracting eq. 1 from 2

$$A_2 - A_1 = (E_2 - E_1) - T (S_2 - S_1)$$

$$\Delta A = \Delta E - T \Delta S$$

Where ΔA is the change in the function A, ΔE is the corresponding change in internal energy and ΔS is the change in entropy of the system.

Suppose the change under reference is brought about reversibly at the constant temperature T and that the heat absorbed is equal to q_{rev} .

Since,
$$\Delta S = \frac{q_{rev}}{T}$$

Hence,
$$\Delta A = \Delta E - q_{rev} \dots\dots\dots(3)$$

From I- law of thermodynamics, $\Delta E = q - w$, it follows that

$$q_{rev} = \Delta E + w_{rev}$$

substituting in eq. (3)

$-\Delta A = w_{rev}$

*i.e. decrease in the function A ($-\Delta A$) in any process at constant temperature gives the maximum work that can be obtained from the system during any change. The function A is therefore termed as the **work function**. This is also referred to as Helmholtz free energy.*

Gibbs free energy

It was introduced by J. Willard Gibbs. The free energy function (G) is defined as follows.

The maximum quantity of energy available to a system during a process of doing a work under the condition of constant temperature and pressure is called Gibbs free energy.

The Gibbs free energy is given by

$$G = H - TS$$

Since, H, T and S are state functions, G is also a state function. For a change at constant temperature, change in G is given as

$$dG = dH - TdS$$

dG is an exact differential. Gibbs free energy is useful to study changes at constant pressure and temperature.

Let the system which undergoes a change of state from (1) to (2) at constant temperature.

We have

$$G_1 = H_1 - T S_1$$

$$G_2 = H_2 - T S_2$$

$$\text{Hence } G_2 - G_1 = (H_2 - H_1) - T (S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S$$

Relation between Gibbs free energy and Helmholtz free energy:

The change in Gibbs free energy is given by

$$\Delta G = \Delta H - T\Delta S$$

we know

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

Also

$$\Delta A = \Delta E - T\Delta S$$

$$\Delta G = \Delta A + P\Delta V$$

Since

$$\begin{aligned} -\Delta A &= w_{rev} \\ -\Delta G &= w - P\Delta V \end{aligned}$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P . Therefore, $-\Delta G$ gives *the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure*. The work other than that due to change of volume is called the **net work**. Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G$$

Hence, $-\Delta G$ is a measure of the maximum net work that can be obtained from a system at constant temperature and pressure. The quantity G is due to Gibbs and is called **Gibbs free energy** or merely as **free energy**.

Variation of Free energy with Temperature, Pressure and Volume:

(a) Variation of G with Temperature and Volume:

Gibb's free energy is defined as

$$G = H - TS \text{ -----(i)}$$

Since, $H = E + PV$,

$$G = E + PV - TS$$

$$\text{On differentiation} \quad dG = dE + PdV + VdP - SdT - TdS \text{ ----- (ii)}$$

From the first law of thermodynamics, $dE = dq + dw$

If the work is due to expansion, then $dw = -PdV$; therefore, $dE = dq - PdV$

$$dq = dE + PdV$$

For a reversible process $dS = dq/T$ or $TdS = dq = dE + PdV \text{(iii)}$

On substituting eq. (iv) in (ii) we get,

$$dG = dE + PdV + VdP - SdT - dE - PdV$$

$$dG = TdS + VdP - SdT - TdS$$

$$dG = VdP - SdT \dots \dots \dots (iv)$$

At constant pressure, $dP = 0$, eq. (iv) becomes, $dG = - SdT$

$$(\partial G / \partial T)_P = -S$$

The rate of change of Gibb's free energy with temperature at constant pressure is equal to decrease in entropy of the system.

At constant temperature, $dT = 0$. Then eq. (iv) becomes, $dG = VdP$

$$(\partial G / \partial P)_T = V$$

Thus the rate of change of Gibb's free energy with respect to pressure at constant temperature is equal to increase in volume occupied by the system.

Further,

$$dG = VdP - SdT$$

At constant temperature, $dT = 0$,

$$\therefore dG = VdP$$

But an ideal gas equation is $PV = nRT$

and
$$V = \frac{nRT}{P}$$

Hence,
$$dG = nRT \frac{dP}{P}$$

On integrating,

$$\int_{G_1}^{G_2} dG = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

Or
$$G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\Delta G = 2.303nRT \log \frac{P_2}{P_1}$$

and

$$\Delta G = 2.303nRT \log \frac{V_1}{V_2}$$

(b) Variation of Helmholtz Free energy (G) with Temperature and Volume:

$$A = E - TS \dots \dots \dots (i)$$

On differentiating, $dA = dE - TdS - SdT \dots \dots \dots (ii)$

We know , $dq = dE + PdV \dots \dots \dots (iii)$

and also $dS = \frac{dq}{T}$ and $Tds = dq \dots \dots \dots (iv)$

substituting eq. (iv) in (iii) $TdS = dE + PdV \dots \dots (v)$

substituting (v) in (ii), $dA = dE - dE - PdV - SdT$

$$dA = - PdV - SdT$$

(i) At constant volume $dV = 0$

$$\therefore dA = - SdT$$

$$(\partial A / \partial T)_V = -S$$

Thus the rate of change of Helmholtz free energy with respect to temperature at constant volume is equal to decrease in entropy of the system.

(ii) At constant temperature, $dT = 0$

$$dA = - PdV$$

$$(\partial A / \partial V)_T = -P$$

Thus the rate of change of Helmholtz free energy with respect to volume at constant temperature is equal to decrease in pressure of the system.

Free energy for criteria for spontaneity:**(i) In terms of Helmholtz free energy:**

We know at constant temperature,

$$dA = dE - TdS$$

We have,

$$-\Delta A = w_{rev}$$

$$dA \leq -PdV$$

At constant volume, therefore, $dA \leq 0$

where, the sign 'equal to' refers to a **reversible process** and the sign 'less than' refers to an **irreversible process**.

i.e. at constant pressure,

when dA is zero ($dA = 0$), then the process is at equilibrium.

When dA is negative ($dA < 0$), then the process is spontaneous.

When dA is positive ($dA > 0$), the process is non-spontaneous (not feasible).

(ii) In terms of Gibbs free energy:

We know

$$G = H - TS$$

$$G = E + PV - TS$$

on differentiating we get

$$dG = dE + PdV + VdP - TdS - SdT$$

But

$$TdS = dE + PdV$$

we have

$$dG \leq VdP - SdT$$

\therefore At constant temperature and pressure

$$dG \leq 0$$

where, as usual, the sign 'equal to' refers to a **reversible process** and the sign 'less than' refers to an **irreversible process**.

i.e. at constant pressure and temperature,

When dG is zero ($dG = 0$), then the process is at equilibrium.

When dG is negative ($dG < 0$), then the process is spontaneous.

When dG is positive ($dG > 0$), the process is non-spontaneous (not feasible).

Maxwell's Relations:

I-law of thermodynamics is

$$dE = q - w = q - PdV$$

For reversible process,

$$q_{rev} = dE + PdV \dots \dots \dots (1)$$

According to II-law of thermodynamics,

$$dS = \frac{q_{rev}}{T} \dots \dots \dots (2)$$

Substituting eq (2) in (1) we get,

$$ds = \frac{dE + PdV}{T}$$

$$TdS = dE + PdV$$

$$\therefore dE = TdS - PdV \dots \dots \dots (3)$$

By definition,

$$A = E - TS$$

On differentiation,

$$dA = dE - TdS - SdT \dots \dots \dots (4)$$

Substitute eq. (3) in (4),

$$dA = TdS - PdV - TdS - SdT$$

$$dA = -PdV - SdT \dots \dots \dots (5)$$

At constant entropy, $dS = 0$	At constant volume, $dV = 0$
-------------------------------	------------------------------

\therefore eq. (5) becomes $dE = -PdV$ or $(\frac{\partial E}{\partial V})_S = -P$ Differentiate the above eq. with respect to S at constant V, $\frac{\partial^2 E}{\partial V \partial S} = -(\frac{\partial P}{\partial S})_V \dots\dots\dots(6)$	\therefore eq. 5 becomes $dE = TdS$ or $(\frac{\partial E}{\partial S})_V = T$ Differentiate the above eq. with respect to V at constant S, $\frac{\partial^2 E}{\partial S \partial V} = (\frac{\partial T}{\partial V})_S \dots\dots\dots(7)$
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From equations 6 and 7,

$$-(\frac{\partial P}{\partial S})_V = (\frac{\partial T}{\partial V})_S \dots\dots\dots(I)$$

Similarly, eq. 5 can be written as

$$dA = -SdT - PdV$$

$$\therefore (\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V \dots\dots\dots (II)$$

By definition $G = H - TS$

$$H = E + PV$$

Hence, $G = E + PV - TS$

On differentiation, $dG = dE + PdV + VdP - TdS - SdT \dots\dots\dots(8)$

Substitute eq. 3 in eq. 8,

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$dG = VdP - TdS$$

As per previous methods the above equation can be written as,

$$(\frac{\partial V}{\partial T})_P = (\frac{\partial S}{\partial P})_T \dots\dots\dots(III)$$

Equations I, II and III are known as Maxwell's relations.

Thermodynamic equation of state:

We know that for reversible process,

$$q_{rev} = dE + PdV \dots\dots\dots(1)$$

And from II-law of thermodynamics,

$$dS = \frac{q_{rev}}{T}$$

$$q_{rev} = TdS \dots\dots\dots(2)$$

Substituting eq. 2 in 1

$$TdS = dE + PdV$$

$$\text{Or} \quad dE = TdS - PdV \dots\dots(3)$$

$$\text{Divide eq. 3 by } dV \text{ at constant } T, \text{ then } \left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \dots\dots(4)$$

According to Maxwell's relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \dots\dots\dots(5)$$

Apply eq. 5 in 4,

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

SO,

$$P = T \left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial E}{\partial V}\right)_T$$

This equation is called as a thermodynamic equation of state. This equation relates P, V and T.

Gibbs-Helmholtz equation – derivation:

Let G_1 , represents the free energy of the system in its initial state at temperature T. Suppose the temperature rises to $T + dT$ where dT is infinitesimally small. Let the free energy at the new temperature be $G_1 + dG_1$.

Now suppose that when the system is in its final state, its free energy is given by G_2 at the temperature T and $G_2 + dG_2$ at the temperature $T+dT$. If the pressure remains constant then,

$$dG_1 = -S_1 dT \dots (1)$$

and

$$dG_2 = -S_2 dT \dots (2)$$

where, S_1 and S_2 are the entropies of the initial and final state of the system respectively.

Subtracting eq. 1 from 2, we have

$$d(G_2 - G_1) = -(S_2 - S_1) dT$$

$$d(\Delta G) = -\Delta S dT$$

As the pressure is constant, therefore

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S$$

Also, since

$$-\Delta S = \frac{\Delta G - \Delta H}{T}$$

hence,

$$\frac{\Delta G - \Delta H}{T} = \left(\frac{\partial(\Delta G)}{\partial T}\right)_p$$

$$\Delta G - \Delta H = T \left(\frac{\partial(\Delta G)}{\partial T}\right)_p$$

or

$$\Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T}\right)_p$$

This equation is known as **Gibbs-Helmholtz equation**. It is applicable to all process occurring at constant pressure.

For a reaction at constant volume the corresponding equation will be,

$$\Delta A = \Delta E + T \left(\frac{\partial(\Delta A)}{\partial T} \right)_v$$

Applications:

- 1) It is applicable for calculation of ΔG for all process occurring at constant pressure.
- 2) It helps to calculate emf of the reversible cell.
- 3) Knowing the values of ΔG and ΔH , the value of ΔS can be measured using the equation, $\Delta G = \Delta H - T\Delta S$

Derivation of Clausius – Clapeyron equation:

Consider the following equilibrium between two phases A and B of the same substance at a given temperature.

$$A_{\text{phase}} \rightleftharpoons B_{\text{phase}}$$

Let, G_A and G_B are the free energies per mole of A and B per mole respectively, then

$$\text{At equilibrium, } G_A = G_B$$

Hence, there will be no free energy change, i.e.,

$$\Delta G = G_B - G_A = 0$$

If the temperature of such a system is raised from T to $T+dT$, the pressure will also have to change from P to $P+dP$, in order to maintain the equilibrium. The relationship between dT and dP can be derived from thermodynamics.

Let the free energy per mole of the substance in phase A at the new temperature and pressure be $G_A + dG_A$ and that in phase B be $G_B + dG_B$, since the two phases are still in equilibrium, hence,

$$G_A + dG_A = G_B + dG_B \dots\dots(1)$$

According to thermodynamics,

$$dG = VdP - SdT$$

This equation gives change of free energy when a system undergoes reversibly a change of temperature dT and a change of pressure dP .

Eq. (1) for phase A may be written as

$$dG_A = V_A dP - S_A dT$$

and for phase B,
$$dG_B = V_B dP - S_B dT$$

Since, $G_A = G_B$, hence from eq. (1)

$$dG_A = dG_B$$

$$V_A dP - S_A dT = V_B dP - S_B dT$$

$$(S_B - S_A) dT = (V_B - V_A) dP$$

$$\frac{dP}{dT} = \frac{(S_B - S_A)}{(V_B - V_A)} = \frac{\Delta S}{\Delta V}$$

Where, V_A and V_B are the molar volumes of the pure substance in two phases A and B respectively. If q is the heat exchanged *reversibly* per mole of the substance during the phase transformation at temperature T , then the change of entropy (ΔS) in this process is given by

$$\Delta S = q/T$$

Hence ,

$$\boxed{\frac{dP}{dT} = \frac{q}{T (V_B - V_A)}}$$

This is **Clausius – Clapeyron equation**.

This eq. gives change of pressure dP which must accompany the change in temperature dT or vice-versa, in the case of a given system containing two phases of a pure substance in equilibrium with each other.

Suppose the system consists of water in two phases, viz., liquid and vapour, in equilibrium with each other at the temperature T

Water (liquid) \rightleftharpoons water (vapour)

Then, q = Molar heat of vapourisation, ΔH_v

V_B = Volume of one mole of water in the vapour state

V_A = Volume of one mole of water in the liquid state

Therefore,
$$\frac{dP}{dT} = \frac{\Delta H_v}{T (V_g - V_l)}$$

Integrated form of Clausis –Clapeyron equation:

For Liquid \rightleftharpoons vapour system, the Clausis-Clapeyron equation can be integrated. The molar volume of the substance in the vapour state is considerably greater than that of a substance in the liquid state. The value of V_l of water at 100°C is negligible when compared with V_g . Hence this equation can be written as,

$$\frac{dP}{dT} = \frac{\Delta H_v}{T V_g}$$

Assuming the gas law is applicable i.e., $PV = RT$ (per mole) then, $V_g = RT/P$,

Hence,
$$\frac{dP}{dT} = \frac{\Delta H_v}{T} \times \frac{P}{RT} = P \frac{\Delta H_v}{RT^2}$$

Or
$$\frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H_v}{RT^2}$$

Assuming ΔH_v remains constant over a small range of temperature, then

$$\int d(\ln P) = \frac{\Delta H_v}{R} \int \frac{dT}{T^2} \dots\dots\dots(2)$$

$$\ln P = - \frac{\Delta H_v}{R} \left(\frac{1}{T} \right) + c$$

$$\text{or} \qquad \qquad \qquad \ln P = - \frac{\Delta H_v}{2.303R} \left(\frac{1}{T} \right) + c' \dots\dots\dots(3)$$

where c and c' are integration constants.

Eq.(3) is evidently the equation of a straight line. Hence the plot of $\log P$ vs $1/T$ should give a straight line with slope = $-\frac{\Delta H_v}{2.303R}$ and intercept = c' . This helps for evaluating ΔH_v .

When eq. (2) is integrated within the limits of pressure P_1 and P_2 corresponding temperature T_1 and T_2 then,

$$\int_{P_1}^{P_2} d(\ln P) = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= \frac{\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Or

$$\boxed{2.303 \log \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)}$$

Applications:

1. It help to calculate ΔH_v if P_1 , P_2 and T_1 and T_2 are known.
2. One can also calculate T_2 if P_1 , P_2 , T_1 and ΔH_v are known.
3. It is used to calculate the effect of pressure on the boiling point of liquid.

Reference Books:

1. A text book of Organic Chemistry - K.S.Tewari, N.K.Vishal, S.N.Mehrotra - Vikas Publishing House (2006).
2. Advanced Organic Chemistry – Bahl and Arun Bahl – S. Chand (1987).
3. Principles of Physical chemistry – B.R. Puri, Sharma and Madan S. Pathanaia– Vishal Publicating Co., (2004).
4. Essentials of Physical Chemistry –Arun Bahl, B.S. Bhal, G.D. Tuli –S. Chand (2014).
5. Modern Organic Chemistry – M.K. Jain, S.C. Sharma – Vishal Publising Co. (2017).