

TEACHER'S CARE ACADEMY KANCHIPURAM



CHEMISTRY

UNIT-I



COMPETITIVE EXAM FOR PG-TRB 2019 – 20

PG TRB CHEMISTRY STUDY MATERIAL -2019

UNIT-1

PERIODIC PROPERTIES

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Need for classification:

It is very difficult to study individually the chemistry of all the elements and millions of their compounds, hence to simplify and systematize the study of chemistry of the elements and their compounds, they are classified into groups (columns) and periods (Series /Rows)

Early attempt to classify the elements:

Dobereiner's Triads, 1829, Dobereiner was the first scientist to classify the elements in some groups. He tried to classify the elements with similar properties in groups of three elements (Triads). He could succeed in making only a few triads.

In the triads of elements the atomic weight of the middle element was the arithmetic mean of the atomic weights of the other two. Some of the triads are as under

Li	Na	K	-	Ca	Sr	Ba	-	P	As	Sb	-	Cl	Br	I
7	23	39	-	40	88	137	-	31	75	120	-	35.5	80	123

Newland's Law of Octaves, 1864

If the elements are arranged in order of their increasing atomic weights, every eighth element had similar properties to the first one like the first and eighth note in music. For example

Li	Be	B	C	N	O	F	Na
Na	Mg	Al	Si	P	S	Cl	K

The main problem with this classification was that inert gases were not discovered at that time and also all the elements could not be classified on this basis.

MENDELEEV'S PERIODIC LAW

(i) **Mendeleev's Periodic Law** - The physical and chemical properties of elements are the periodic function of their atomic weight

(ii) Characteristic of Mendeleev's Periodic Table –

(a) It is based on atomic weight. (b) 63 elements were known, noble gases were not discovered. (c) 12 Horizontal rows are called periods. (d) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table. (e) Each group upto VIIth is divided into A & B subgroups. 'A' sub groups element are called normal elements and 'B' sub groups elements are called transition elements. (f) The VIIIth group was consists of 9 elements in three rows (Transition metals group). (g) The elements belonging to same group exhibit similar properties.

(iii) Merits of Mendeleev's periodic table -

(a) Study of elements - First time all known elements were classified in groups according to their similar properties. So study of the properties become easier of elements.

(b) Prediction of new elements - It gave encouragement to the discovery of new elements as some gaps were left in it. Sc (Scandium), Ga (Gallium), Ge (Germanium), Tc (Technetium) were the elements for whom position and properties were defined by Mendeleev even before their discoveries and he left the blank spaces for the min his table.

e.g.- Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element discovered later was named Germanium. Similarly other elements discovered after Mendeleev periodic table were. Eka aluminium-Gallium(Ga), Eka Boron - Scandium (Sc), Eka Silicon -Germanium(Ge), Eka Manganese -Technetium(Tc).

(c) Correction of doubtful atomic weights –Correction were done in atomic weight of some elements.

Atomic Weight =Valency \times Equivalent weight. Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent ($V=3$), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent ($V= 2$). So, the weight of Be became $2 \times 4.5 = 9$ and there was a space between Li and B for this element in Mendeleev's table.– Corrections were done in atomic weight of elements are –U, Be, In,Au, Pt.

(iv) Demerits of Mendeleev's periodic table -

(a) Position of hydrogen - Hydrogen resembles both, the alkali metals (IA) and the halogens (VIIA) in properties so Mendeleev could not decide where to place it. (b)

Position of isotopes - As atomic weight of isotopes differs, they should have placed in different position in Mendeleev's periodic table. But there were no such places for isotopes in Mendeleev's table.

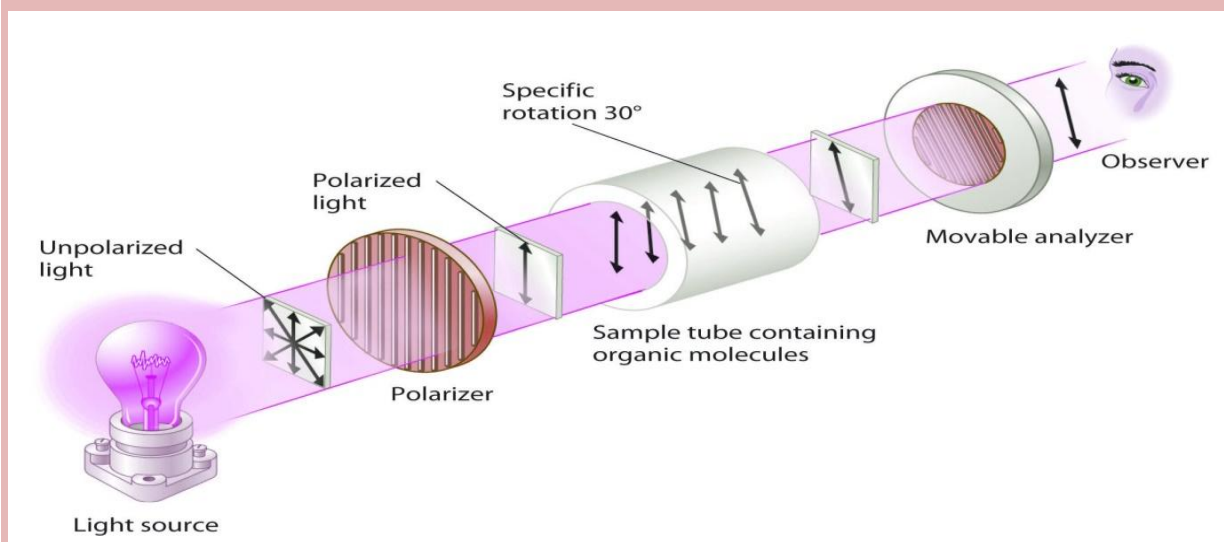
(c) Anomalous pairs of elements - There were some pair of elements which did not follow the increasing order of atomic weights.eg. Ar and Co were placed before K and Ni respectively in the periodic table, but having higher atomic weights.

Ar	K
39.9	39.1
Te	I
127.5	127
Co	Ni
58.9	58.6

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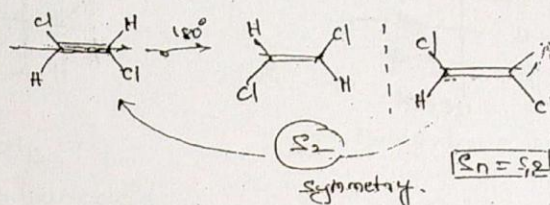
CHEMISTRY (Unit – II)



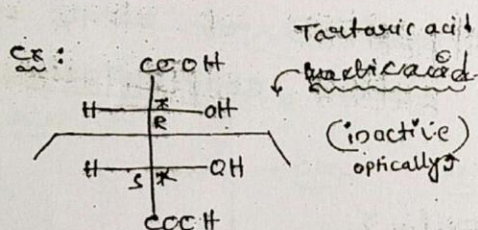
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3). S_n -Symmetry Element:

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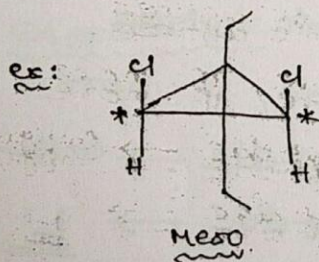


molecules having plane of symmetry \rightarrow Optically inactive
without plane of symmetry \rightarrow Optically active.



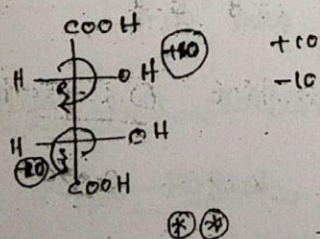
$S_n = C_n + \sigma + i^n$
in rotation followed by reflection

meso-compound: molecule having plane of symmetry as well as asymmetric centre. (chiral)



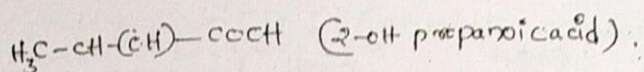
Meso-tartaric Acid

has Internal Compensation:

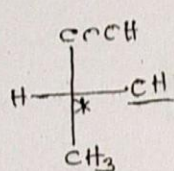
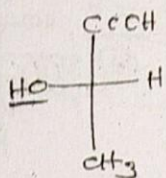


Due to Internal compensation of rotations, meso-comp's Optically inactive.

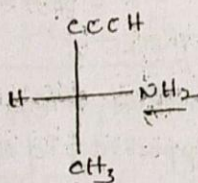
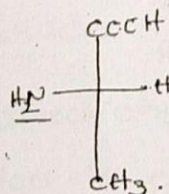
ex:



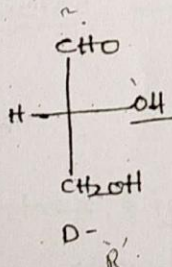
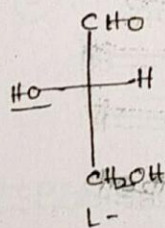
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D-Lactic acid
R'L-lactic acid
S'

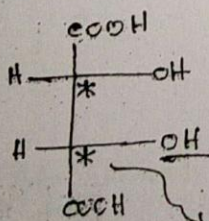
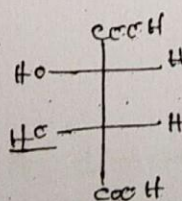
*

If Comp have 1 chiral centre
Enantio Relation ship. \Rightarrow DLAlanine:D-alanine
R'

L-Alanine

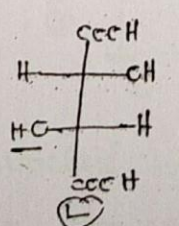
Glyceraldehyde:D-
R'

L-

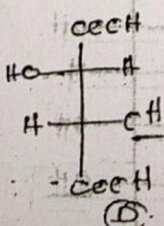
2-chiral centres:D-meso
tartaric acidBottom most
chiral centre.

L-meso

tartaric acid.

active Tartaric acids

(L)



(D)

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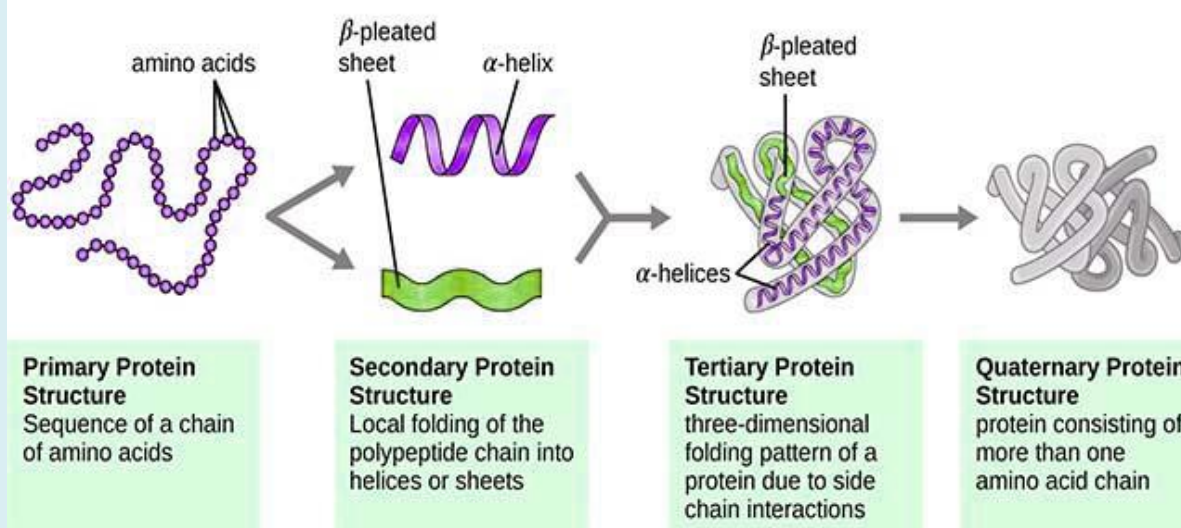
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CHEMISTRY

(UNIT -III)

Structure of Proteins



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PG TRB

UNIT-III

UNIT 9

CHEMISTRY

Organic Reaction Mechanism :

According to Gibbs free energy

$H-TS$ (or) $\Delta G = \Delta H - T\Delta S$. For the Reaction to take place spontaneously ΔG should be $-ve$, and Enthalpy change ΔH should be $-ve$ and Entropy change ΔS should be $+ve$.

For Spontaneous process $\Delta G = -ve$
 $\Delta H = -ve$
 $\Delta S = +ve$

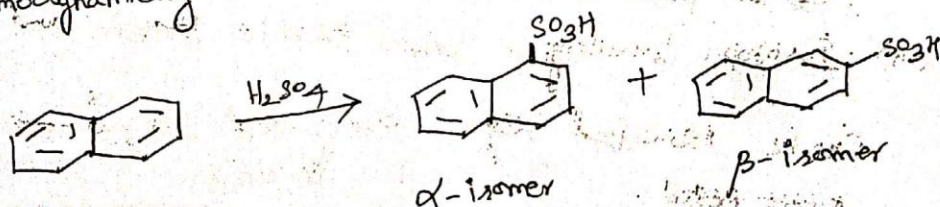
Any Reactions in which the Reactant are all liquids, and one or more parts of the products is gas. The Reaction is Thermodynamically favoured by the increased entropy.

The Reaction yielding products involving

lower free energy of activation are called Kinetically Controlled Reaction.

A different set of products more slowly but corresponding to lower free energy may be obtained such Reactions are called Thermodynamically Controlled Reaction.

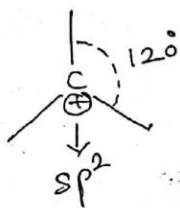
Example :



α -isomer is formed faster than β -isomer. But α -isomer is less stable than β -isomer which does not involve repulsive forces between the SO_3H group at C_1 and the Hydrogen at C_2 . α -isomer is Kinetically Controlled product whereas β -isomer is

Reaction Intermediates

1. Carbocations : The Carbon with Trivalent bond contain even no. of electrons and carry +ve charge.



Structure : Trigonal Coplanar

Bond angle : 120°

Hybridisation : sp^2

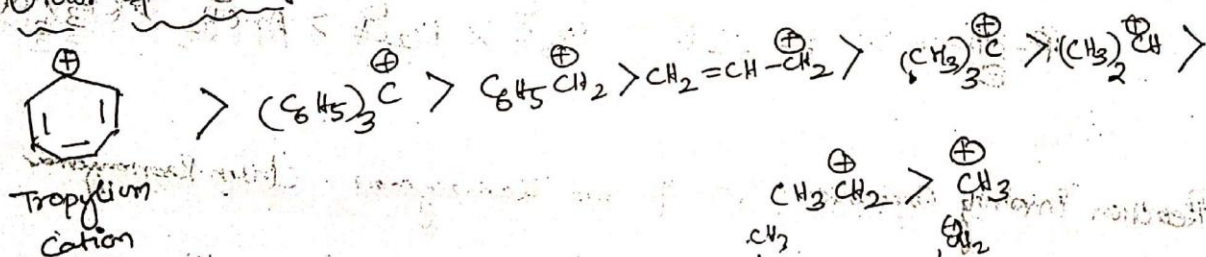
No of e^- : 6

Stability : If an electron Releasing group such as Alkyl group is adjacent to the carbon atom then Stability will Increase

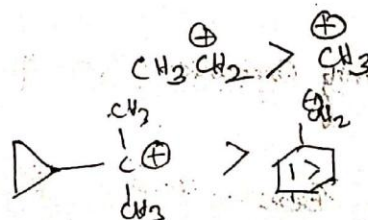
If an electron withdrawing group such as CN , NO_2 is adjacent to the carbon atom then stability will decrease.

Stability can be explained by Resonance. Thus basic requirement for Carbocations is stable and it should be planar and effective delocalisation should occur.

Order of Stability :- Tropylium cation is highly stable than Triphenyl cation



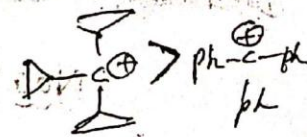
Reaction involving Carbocations : $NO_2 \Rightarrow$



(i) Baeyer Villiger Oxidation (ii) Beckmann Rearrangement

(iii) pinacol pinacolone (iv) Wagner Meerwein Rearrangement,

(iv) Markovnikov Rule (v) Demjanov Rearrangement..



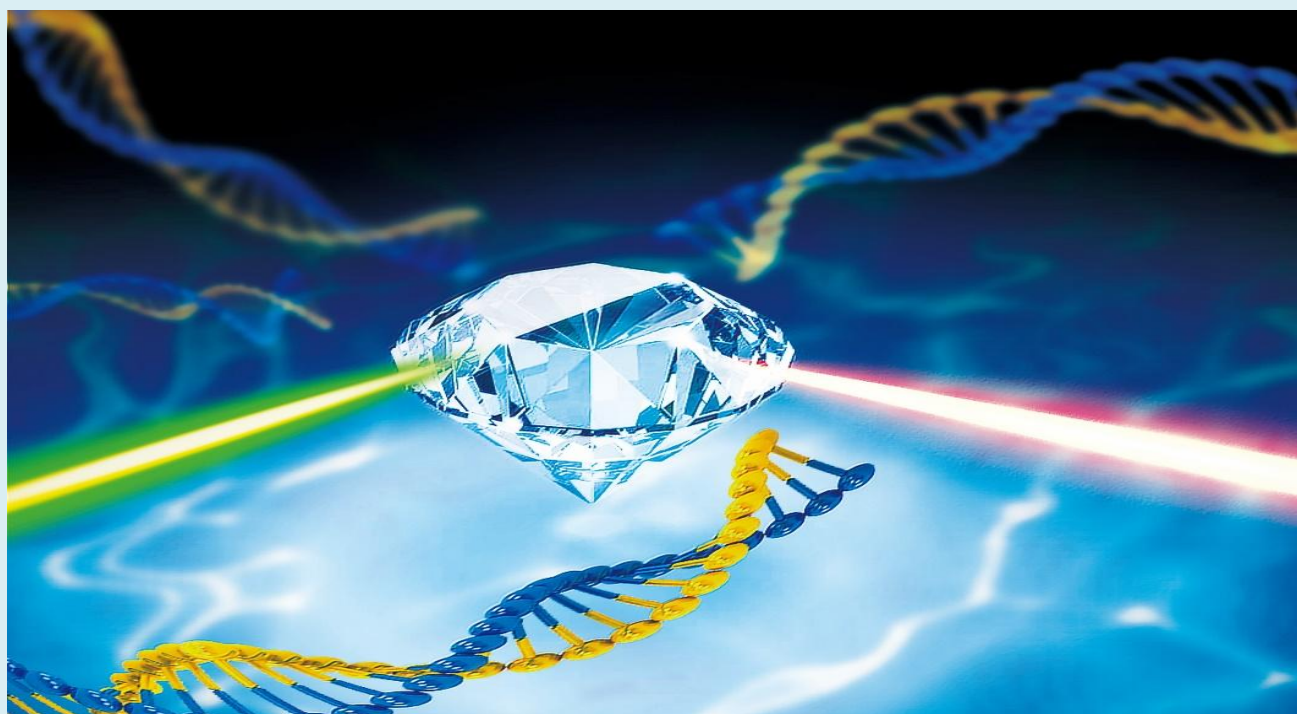
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CHEMISTRY

(Unit – VII)



COMPETITIVE EXAM

FOR

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Determination of G state term:

(L-S Coupling)

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$L \rightarrow$ Resultant orbital angular momentum.

l = orbital angular momentum of single e^-

$$l_1 + l_2 + l_3 + l_4 \dots = L$$

\Rightarrow The (l) defines the state of single e^-

(L) defines the state of an atom/ion as a whole

$$l = 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5$$

$$s \quad p \quad d \quad f \quad g \quad h$$

$$L = S \quad P \quad D \quad F \quad G \quad H$$

\Rightarrow The (L) value are obtained by summation of (l) values.

ex: p^2 - system.

$$m_l = \begin{array}{|c|c|c|} \hline +1 & 0 & -1 \\ \hline 1 & 1 & \\ \hline \end{array}$$

$$l = (1) \quad \text{or } p = L$$

d^2 - system:

$$m_l = \begin{array}{|c|c|c|c|c|} \hline +2 & +1 & 0 & -1 & -2 \\ \hline 1 & 1 & & & \\ \hline \end{array}$$

$$l = (2) \quad (2)_F$$

d^7 - system:

$$m_l = \begin{array}{|c|c|c|c|c|} \hline +2 & +1 & 0 & -1 & -2 \\ \hline 1 & 1 & 1 & 1 & 1 \\ \hline \end{array}$$

$$l = (3) \quad L = (3)_F$$

$S \rightarrow$ Resultant spin angular momentum.

$$S = s_1 + s_2 + s_3 + s_4 + \dots$$

$s \rightarrow$ spin angular momentum of single e^- .

$$S = \frac{1}{2} \times n \quad (\because n \rightarrow \text{no. of unpaired } e^-)$$

(*)

$$S = \frac{n}{2}$$

\Rightarrow The (s) defines the state of single e^- .

(S) defines the state of an atom/ion as a whole.

$[2S+1] \rightarrow$ maximum spin multiplicity.

(*)

$$2S+1 = n+1$$

(*)

$$L + S = J$$

$(J \rightarrow \text{Resultant } ^{\circ} \text{ angular momentum})$

(or)

(Resultant total quantum number)

J is always \oplus ve. & never be 0.

It can take values between

$$(L+S \text{ to } L-S)$$

(maximum J value) (minimum J value)

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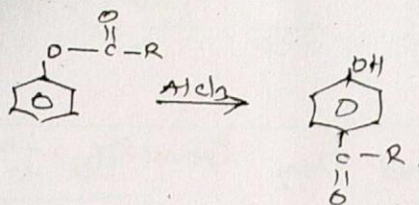


CHEMISTRY (Unit – VIII)



**COMPETITIVE EXAM
FOR
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FRIES



This can be carried with UV light.

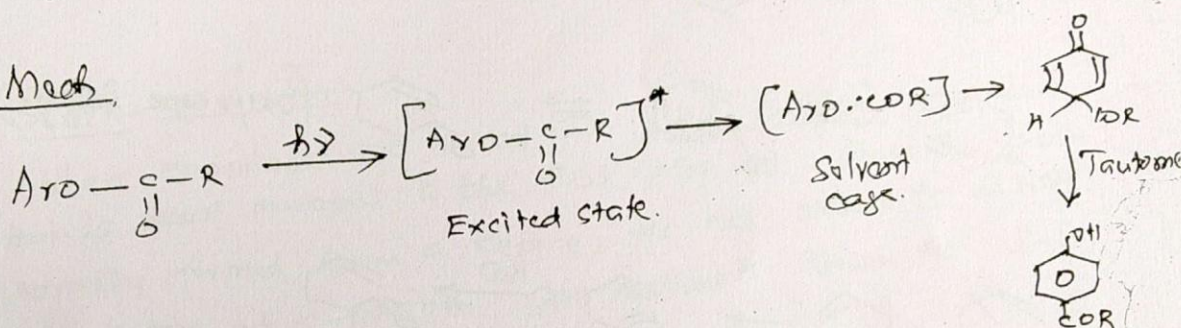
Phenolic esters can be rearranged by heating in Friedel Crafts catalysts.

O & P acylophenols may be produced.

Low temp. generally favours para prod.

High " " " " ortho " "

Mech.

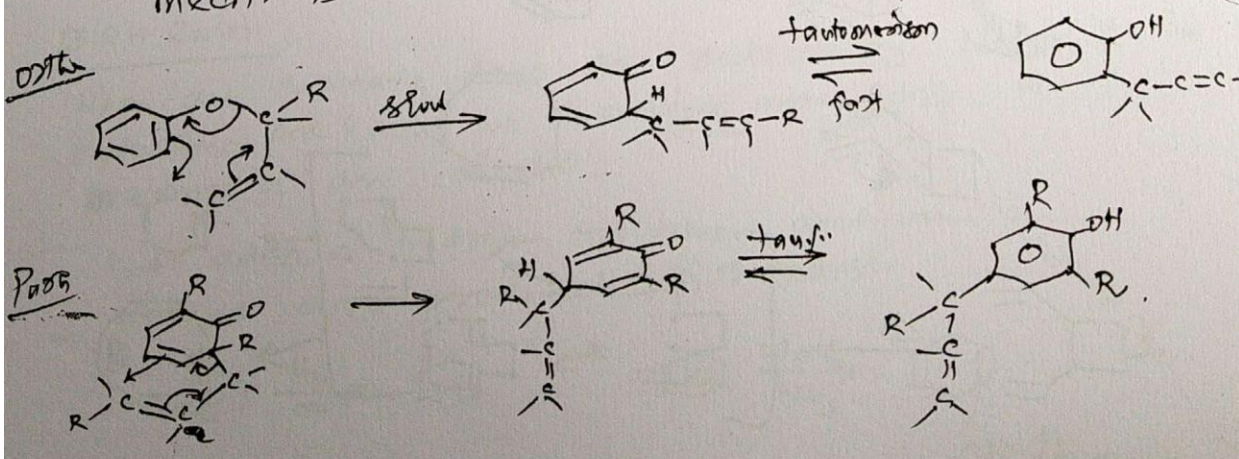


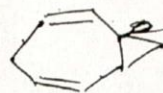
Claisen - Rearr.

Allyl aryl ethers, when heated rearrange to α -allylphenols. In a vac. is called Claisen Rearr. If both ortho positions are filled the allyl group migrates to para position. (Para Claisen Rearr.)

Migro to meta has not been observed.

Mech. is concerted [3,3] sigmatropic rearrangement

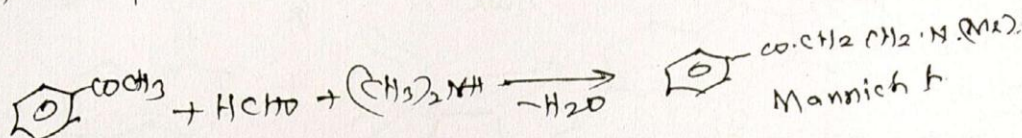




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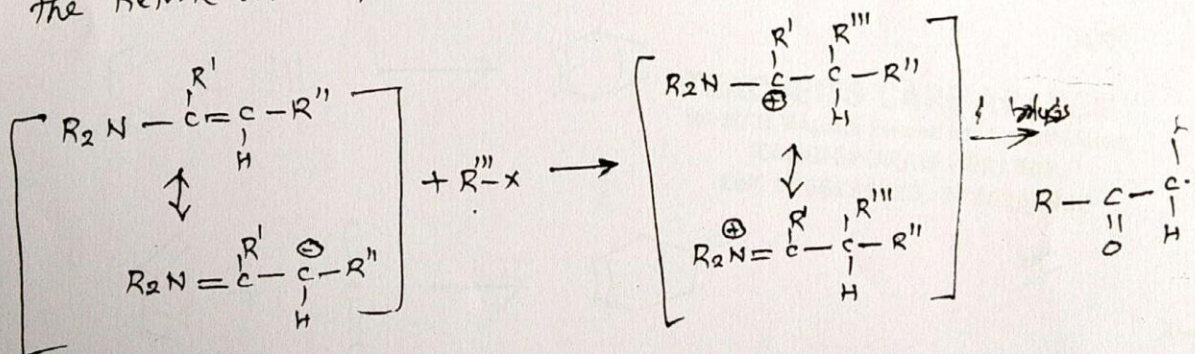
Mannich Rxn.

1° & 2° amines condenses with formaldehyde and a Comp. Containing atleast one active hydrogen atom to replace its active hydrogen by a substituted aminomethyl group.



Stork - Enamine Rxn:

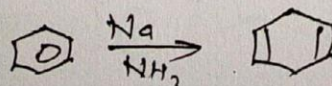
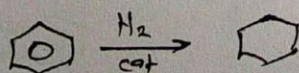
When enamines are treated with alkyl halides, an amino that is ~~analogous~~ analogous to the first step. Since the amino normally formed from a ketone, the net result is alkylating the ketone at α -position. The method is known as S-E



BIRH Redn.

When an aromatic rings are reduced by Na or K in presence of an alcohol. These reductions are known as dissolving metal Redn. w/o presence of an alcohol.

1,4 addn. of hydrogen takes place and non-conjugated dienes are produced. Birch Redn.



cis/trans



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CHEMISTRY (Unit – IX)



**COMPETITIVE EXAM
FOR
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Determination of solubility and solubility Product.

The solubilities of sparingly soluble salts such as AgNO_3 , AgCl , BaSO_4 , PbSO_4 can't be determined by chemical methods. But this can be done by conductivity measurements.

Let us calculate the solubility of AgCl at 25°C . The salt is washed well with conductivity water. It is then suspended in conductivity water, warmed and cooled to 25°C . A very minute quantity of salt will pass into the solution. The conductance of the solution is determined. Conductance of water also determined. The difference $<>$ the two is multiplied by cell constant, gives specific conductance of the solution due to the dissolved salt.

Let the value = 2.5 m^{-1} .

Soln. of AgCl = $x \text{ mole / cubic metre}$.

Conc. of AgCl in aq. soln. = $x \text{ mole m}^{-3}$.

\therefore molar conductance of the soln = Λ_m



comparing eqns. (1) & (2) it becomes

$$-nFE = -nFE^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nFE = -nFE^\circ + RT \ln \frac{1}{[M^{n+}]} \rightarrow (3)$$

(\because The activity of solid metal = 1)

Dividing the above eqn. (3) by $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \rightarrow (4)$$

When $R = 8.314 \text{ J/K/mole}$ $F = 96500 \text{ Coulombs}$

$T = 298 \text{ K (25}^\circ\text{C)}$ the above eqn. becomes,

$$\boxed{E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]} \rightarrow (5)$$

The above equation is known as 'Nernst Equation for single electrode Potential'.

**TEACHER'S CARE ACADEMY
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CHEMISTRY
(Unit – X)



COMPETITIVE EXAM
FOR
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1

The UV region between 200 nm - 400 nm.

2. When a molecule absorbs UV radiation of frequency, the e^- in that molecule undergoes transition from a lower to a higher energy level & the energy is

$$E = h\nu$$

$$E_1 - E_0 = h\nu$$

The absorption spectrum is not a discrete line because electronic absorption is superimposed on rotational & vibrational sublevels.

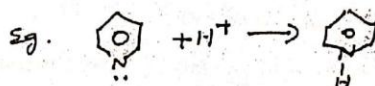
3. The change in energy values for different transitions are

$$n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* < \sigma \rightarrow \sigma^*$$

(a) $n \rightarrow \pi^*$ transitions: This type of transition is shown by unsaturated molecule which contains atoms such as O, N, S. Exhibits weak band. In aldehyde & ketones, the band occurs at in the region 270 - 300 nm.

\Rightarrow Carbonyl compounds having double bonds separated by 2 or 3 single bonds exhibit the bands in the region 300 - 350 nm.

\Rightarrow When H atom is replaced by methyl group in aldehyde, this results in a shift to shorter wave lengths.



In acidic medium, the $n \rightarrow \pi^*$ transition will not appear because the lone pair of e^- on N is not available.

(b) $\sigma \rightarrow \sigma^*$ transition: occur in compounds where all the electrons are involved in single bonds & there are no lone pairs of electrons.

Egy. required for $\sigma \rightarrow \sigma^*$ is very large.

This transition absorbs at in the region (120 - 135 nm). No commercial spectrophotometer operates at this region 180 - 200 nm, so $\sigma \rightarrow \sigma^*$ normally not observed.

(c) $n \rightarrow \sigma^*$ transition: Saturated compounds with lone pair of electrons undergo this transition. $(CH_3)_3N$ $\lambda_{max} = 227$ nm. for $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ for this molecule occurs at 99 nm.

~~copy~~

Raman Spectroscopy.

~~Scattering~~

When a monochromatic light is ~~passed~~ irradiated on solid, liq. or gaseous state of a substⁿ - some additional scattered lines of same frequency that of frequency of incident light obtained. These additional lines are Raman lines. The line wave length $>$ that of the incident wave length \Rightarrow Stoke's lines. wave length of line is $<$ that of the incident wave length \Rightarrow anti Stoke's line.

$$\Delta\lambda = \lambda_i - \lambda_s$$

$\Delta\lambda$ is +ve for Stoke's line
 $\Delta\lambda$ is -ve " anti " "

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Raman Spectra

1. Scattering of light by the vibrating molecules.
2. Polarizability of the molecule will decide ^{Raman} active or inactive.
3. water can be used as a solvent.
4. Sometimes, photochemical reactions takes place & this creates difficulties.
5. Optical systems are made of glass or quartz.
6. Substances should be pure and colourless.
7. vibrational frequencies of large molecule can be measured.
8. Homonuclear diatomic molecules are inactive.

IR spectra
absorption of light.

change in dipole moment shows IR active or inactive.

water can't be used.

don't take place.

optical systems are made of CaF_2 , NaBr etc.

no conditions.

can't be measured.

not active.

