Code :- 18KP3CHELCH3

Research methodology & current trends in Chemistry

Unit - III

Sec - A

5×2 = 10

1. What is chromatography?
2. Give the classifications of chromatography?
3. Give the principle of ion Exchange and affinity chromatography.
4. What is solvent Extraction?
5. Applications of Solvent Extraction.

Sec - B

4×5 = 20.

1. define Gas chromatography?
2. Explain briefly TLC ?
3. Give the basic principle of ion Exange chromatography?
4. Explain Affinity Chromatography?

Sec - C

2×10 = 20

1. Explain solvent Extraction?
2. Explain briefly liquid chromatography?

Unit - III

HYPHENATED TECHNIQUES

Gas chromatography :

Gas chromatography is quite similar to column chromatography Except that a gas is used to the mobile phase instead of a liquid. Gas - solid chromatography is based upon selective adsorption on a solid, whereas gas-liquid chromatography is based upon the partition between the gas and immobile liquid phase.

The main advantages of gas chromatography :-

- The technique has strong separation power and even complex mixtures can be resolved into constituents.
- The sensitivity of the method is quite high.
- The analysis is completed in a short time
- The cost of instrument is relatively low and its life is generally long.

Principle of Gas chromatographic separations.

when a gas or vapour comes in contact with an adsorbent. certain amount of it gets adsorbed on the solid surface.

The gas chromatographic separation is carried ou in adsorbent filled as the stationary phase. The adsorbent filled are picked packed in the form of fine size graded powder, whereas the liquids are either coated as fine films on the coloumn wall or first coated over an inert size graded porous support such a fire brick powder followed by packing in the coloumn. A gas serving as a mobile phase flows continuously through the coloumn. it is known as carrier gas. The sample is introduced in the vapour form at the carrier gas entrance end of the coloumn; Different components of the Sampl are adsorbed on the stationary phase to differen extents depending upon their distribution co-efficient.

Thin layer chromatography:-

It is also called surface chromatography or open coloumn chromatography. It is a type of adsorption chromatographic technique of separation of mixtures of compounds and identification of the of the constituents

Principle of Thin layer chromatography:-

Different compounds will have different solubilities and adsorption to the two phases between which they are to be partitioned.

Applications:

(i) Separation of multicomponent pharmaceutical formulations.

(ii) in food and cosmetic industry. TLC method is used for separtion and identification of food, colors, preservatives, sweetening agent.

Liquid chromatography

LC is an analytical chromatographic technique that is useful for separating ions or molecules that are dissolves in a solvent.

principle of liquid chromatography:-

Interactions of moleculer size (size exclusion chromatography, ion exchange chromatography, hydrophobicity, specific binding interactions

Applications :-

It is used to separate proteins, nucleic acids, (or) small molecules in complex mixture.

Ion - Exchange Chromatography:

Ion chromatography separates ions and polar molecules based on their affinity to the ion exchanger

Principle of ion Exchange chromatography :-

In Cation Exchange chromatography positively charged molecules are attracted to a negatively charged solid support.

Converesely. in anion exchange chromatography negatively charged molecules are attracted to a positively charged solid support

(ie) ionic interaction between oppositely charged ionic groups in the sample molecule. It is the basic principle of ion Exchange chromatography.

Applications :-

- softening of hard water
- Demineralization of water
- To analyse base composition of nucleic acid
- To concentrate the metal ions in the Sample
- To measure the additives in food and drug sample
- To separate protein mixtures

Affinity chromatography :-

Affinity chromatography is a method for separating a biomolecule from a mixture, based on a highly specific macromolecular binding interaction between biomolecule and another Substances

principle of Affinity chromatography :-

(i) Inject a sample into an initially equilibrated affinity chromatography column

(ii) Only the substances with affinity for the ligand are retained in the Column.

(iii) other substances with no affinity for the ligand are eluted from the coloumn.

(iv) The substances retained in the coloumn can be eluted from the coloumn by changing p^{H} or salt or organic solvent concentration of the eluent.

Applications :-

* It is used for isolation and purification of all biological macromolecule.

* To reduce a amount of substance in mixture

* It is used to nucleic acid purification.

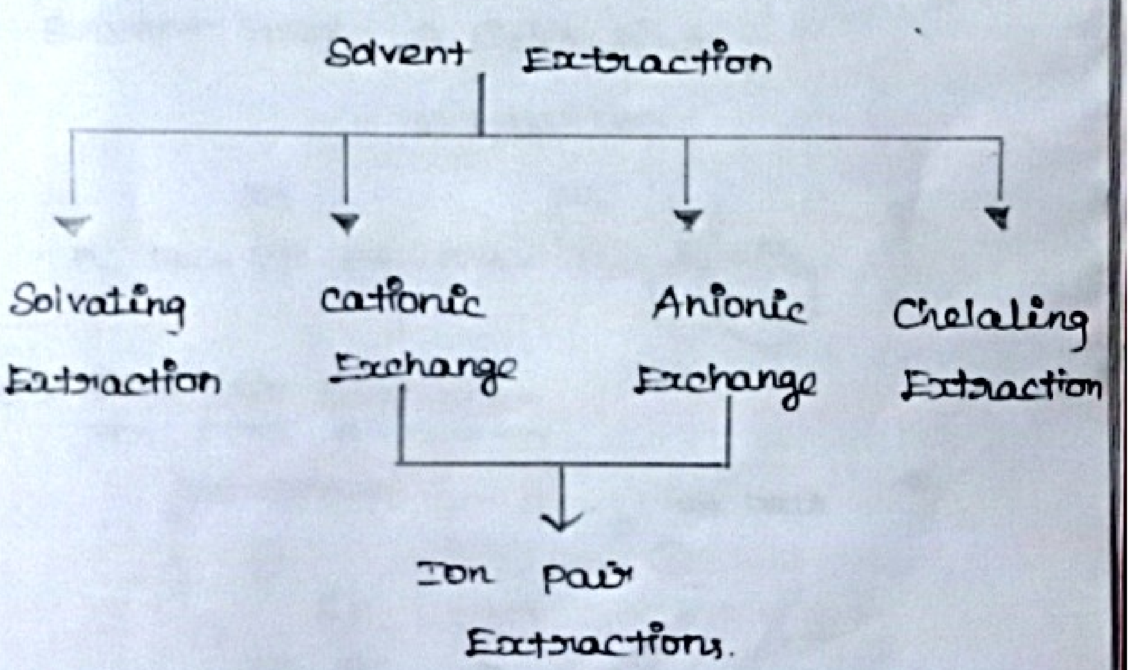
Solvent Extraction

Liquid liquid extraction also known as Solvent extraction and partitioning, is a method to Separate Compounds or metal Complexes. based on their relative Solubilities in two different immiscible liquids.

Principle of Solvent extraction:

In Solvent Extraction, two immiscible liquids are shaken together. The more polar solutes dissolve preferentially in the polar solvent and the less polar solutes in the less polar solvent. In this experiment, polar substance are preferentially dissolve in the polar solvent. Non-polar substances are preferentially dissolve in the non-polar solvent.

Classification of Solvent Extraction:



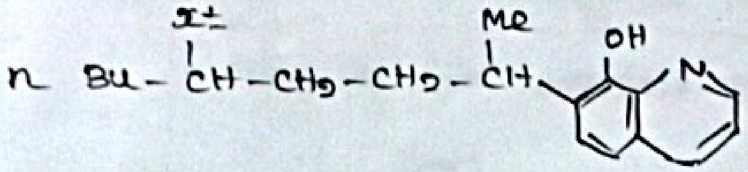
(i) Solvating Extraction:-

Solvent used :- 1) Tri Butyl phosphate
2) Tri octyl phosphine oxide
3) Methyl iso Butyl Ketones

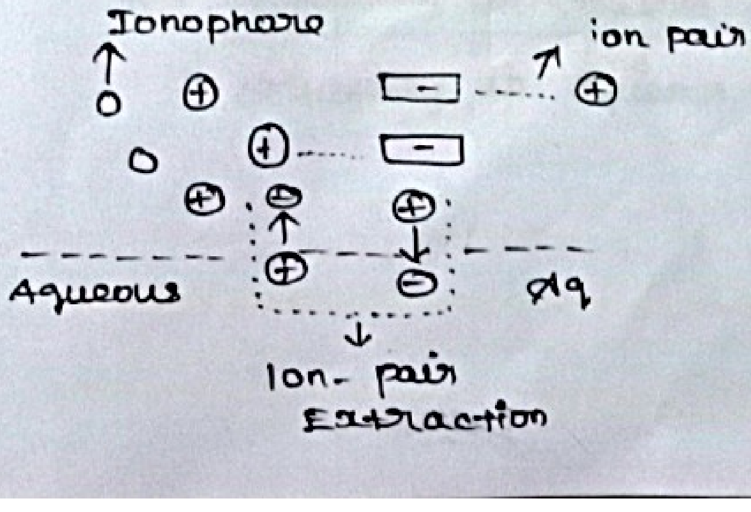
- Solid-Liquid Extraction
- Contact of solute with the liquid phase
- Separation of the liquid phase from solid phase

(ii) Chelating Extraction:

Solvent used : 1) Lix 63, Lix 65
2) Kelex 100.



(iii) Ion-pair Extraction:



Theory of Solvent Extraction:-

When a solution is placed in a separatory funnel and shaken with an immiscible solvent, solutes often dissolve in part into both layers. The Components are said to 'partition between the two layers or "distribution themselves" between the two layers. when equilibrium has established, the ratio of concentration of solute in each layer is Constant for each system, and this Can be represented by a value K (called the partition Co-efficient)

$$K = \frac{\text{Molarity in Organic phase}}{\text{Molarity in aqueous phase}}$$

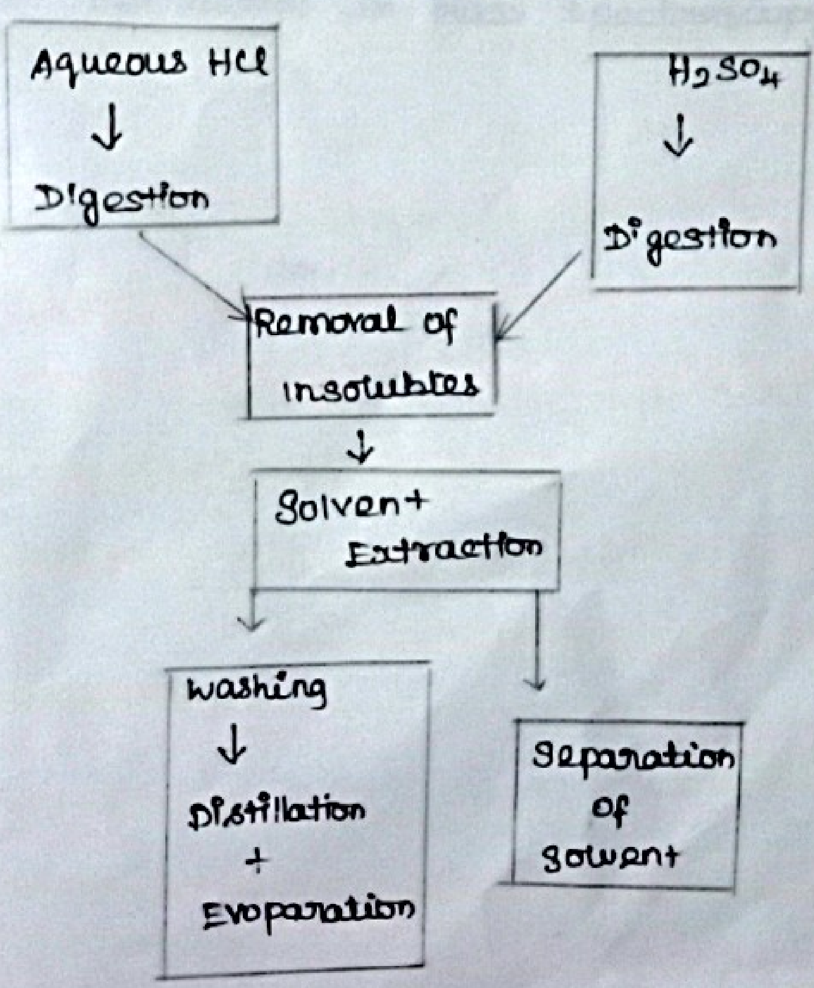
(or)

$$K = \frac{\text{Solubility in Organic phase}}{\text{Solubility in aqueous phase}}$$

Instrumentation of Solvent Extraction:

Instrument required

- Mobile phase reservair
- pump
- Injectar
- coloumn
- Detector
- Data system



Applications

(i) Extraction in Hydrometallurgy

(ii) Extraction in Nuclear chemistry

(iii) Extraction in Biofuel Separation

(iv) Extraction in wastewater treatment

(v) Extraction in pharmaceutical Biochemistry

(vi) Extraction in Mass spectroscopy.

Unit - IV

sec - A

5×2 = 10.

1. What are the top ten use of nanotechnology?
2. What can be major applications of CNT?
3. What is nanotechnology?
4. Define : carbon clusters?
5. What is larger and smaller fullerenes?

sec - B

4 × 5 = 20

1. What are the nano particles property useful for diagnostic applications?
2. Highlight the advantages of electro deposition for the synthesis of nano scale materials.
3. Explain briefly C_{60} (Fullerenes).
4. Applications of nano wires?

sec - C

2 × 10 = 20

1. Explain briefly semiconductor quantom dots
2. Explain the Applications and properties of Gold Nano Particles?

Unit - IV

Nano chemistry:.

Definition:

Nanomaterials can be defined as materials possessing, at minimum, one external dimension measuring 1-100 nm. These materials can have different physical and chemical properties to their bulk-from counterparts.

Size effect:

The bulk properties of materials often change dramatically when reduced to nano scale dimensions starting roughly at 100 nm and below, materials break a size barrier below which quantization of energy for the electrons in solids becomes relevant.

Importance of Nano materials:-

(i) Nano phase Ceramics

(ii) Nano structured semiconductors

(iii) Nano sized metallic powders.

Unique properties of Nano particles :-

- Stable materials turn combustible (Aluminium)
- Insulators become conductors (silicon)
- Solids turn to liquids at room temparature (Gold)

Carbon clusters:

carbon clusters are produced by the gas are discharge method, were strong heat convection flows up sublimated carbon atoms immediately. and the reaction time is restricted

Nature of carbon bond in carbon clusters:

C has 4 valence electrons, so, C can form 4 covalent bonds to satisfy a full valence shell.

These 4 covalent bonds yield lots and lot of possible combinations

FULLERENES

A fullerene is a pure carbon molecule compound of at least 60 atoms of carbon because a fullerene takes a shape. it is a allotropic of Carbon.

Discovery of fullerenes:-

* The research for certain linear molecules Carbon normally discovery of carbond found in the interstellar region called cyano polyenes.

* The major discovery was not the detection of cyanopolyenes. But not the usually abundant Species C_{60}. which dominated the mass spectrum under certain clustering Conditions.

There were other heavior cluster top. It is particularly unreactive as compared to the lower Clusters. Reactivity and photo fragmentation Studies showed that the 60 atom. Cluster is extremely stable. The observed chemistry can be explained if one assumed that the graphitic sheets transform into a hallow chicken-wire cage similar to the atom of buckminster

Super conductivity in C_{60}

The C_{60} fullerenes has a fcc lattice with a lattice Constant of 14.17 Å at room temparature. fullerene molecule is highly electronegative and form doped Compounds with alkali metals These doped fullerenes molecules are super Conductors at temparature below 20-40K. K_rC_{60} and Rb_3C_{60} shows superconductivity with the Consot Tc of 18K and 28K. Not only K and Rb doped superconductors have M_3C_{60} stoichiometry, indeed all the alkali doped Superconductors have same M_3C_{60} stoichiometry. However, Tc increases from 17 to 28 with increase in x from zero to 1 in $K_{c-x}Rb_x$. interestingly. $Rb_3 60$ compound Tc can even increases to 40K. Although at atmospheric pressure $Cs_3 60$ Compound is both insulating and magnetic. Recently hole doped fullerenes system $C_{60}/CHBr_3$ has exhibited greatest critical temparatures, $T_c = 117$ K at ambient pressure for an Organic SuperConductor.

Field effect doping techniques have been expoited to prepare superconducting fullerenes. The maximum Tc of 52 K for 3 ± 8 5 hole per C_{60} which is almost five time higher than for electron doping has been absorved. instead of preparing the superconductor in powered from fullerene nanochisiter by pottassium interaction has been prepared in the present article a review of superconductive fullerenes derivatives is described.

larger fullerenes:- and smaller fullerenes

Fullerenes with fewer than 60 carbon atoms have been called lower fullerenes. and those with more than 70 atoms higher fullerenes.

Carbon nano tubes

Carbon nanotubes (CNT) are cylindrical molecules that consist of rolledup sheets of single-layer carbon atoms. They can be single walled with a diameter of less than 1 nanometer or multi walled consisting of several concentrically interlinked nanotubes, with diameters reaching more than 100 nm.

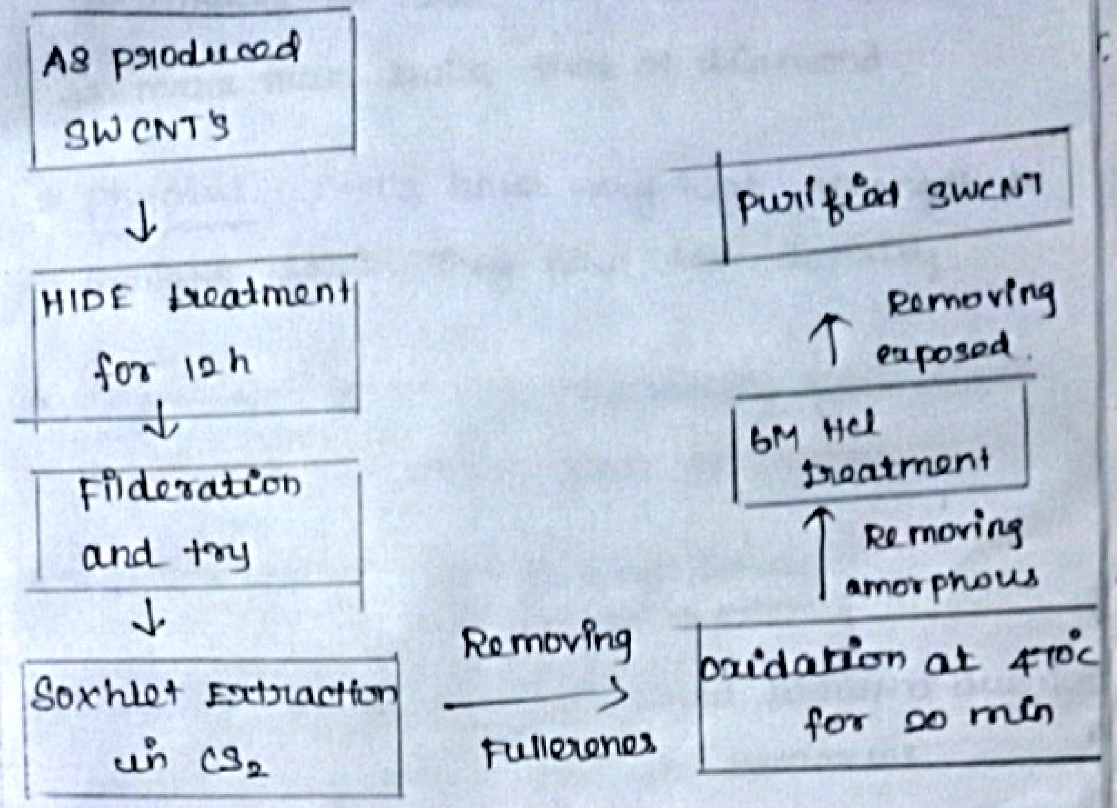
Synthesis of carbon-nano tubes:

There are several techniques that have been developed for fabricating CNT structures which mainly involve gas phase processes. Commonly, three procedures are being used for producing CNTs: (i) The chemical vapor deposition (CVD) technique

(ii) The laserablation technique

(iii) The carbon arc-discharge technique

purification of carbon-nano tubes



Properties of Carbon nano-tubes :-

Strength :-

- * The strongest and stiffest materials.
- * Standard single walled carbon nanotubes can withstand a pressure up to 24GP without deformation

Kinetic : * Stable kinetic energy.

Electrial :- moderate semiconductor

- **Thermal:** Carbon nanotubes are very good conductors of heat. Their thermal Conductivit is more than twice that of diamond.

- **physical:-** CNT's have very high strength to weight ratio. They have low density.

- **Chemical:-** CNTs are chemically more inert compared to other form of carbon.

Applications of Carbon Nano Tubes:-

- Carbon nanotubes can store lithium due to which they canbe used in batteries
- They are used in the tips for atomic force microscope probes.
- They are being used to develop flat planel displays for television and computer monitors
- They are being used to develop light weight shield for electromagnetic radiation.
- They are used in chemical sensors to detect gases.

Nano wires :- properties :

* Actually the magnetic properties of nanowires depend on the wire diameter and aspect ratio

* It have a electrical property.

* and have a optical and mechanical Property

* Silicon nanowheries Coated with SiC shao Stable and photoluminescene at room temparature

Applications of Nano-wires:

* High quality single crystal wires with nearly perfect surface

* Best cross-section for surround gate

* Very cost effective material synthesis

* Nanowires thus represent the best-defined class of nanoscale building blocks, and this precise Control over by key variables has correspondingly enabled a wide range of devices and integration Strategiés to be pursued.

Semiconductor Quantum dots:

QDs are nanoscale materials cluster composed of 10^2-10^5 atoms. The size of the QDs is orders of magnitude larger than a typical atomic radius, yet small enough to provide Quantum confinement of electrons and holes in all three spatial dimensions. Consequently, they are also referred to as artificial atoms.

Applications for quantum dots:

* It is used as solar cells.
* It is used to LEDs. lasers.
* It is used to single-photon sources.
* Quantum computing, cell. biology research and medical imaging

Nano medicine:

Nano medicine is the medical application of nanotechnology. Nanomedicine ranges from the medical applications of

Nanomaterials and biological devices to nano electronic biosensors, and even possible future applications of molecular nanotechnology such as biological machines.

Applications:

* Food and drug administration to treat breast cancer, non-small cell lung cancer. and pancreatic cancer.

* The nanocrystal components allow for increased drug solubility and dissolution rate, leading to improved absorption and high bioavailability

* It is used blood purification.

* Nanotechnology may be used as part of tissue engineering.

Gold Nano particles :-

it is small gold particles with a diameter of 1 to 100 nm which, once dispersed in water are also known as colloidal gold.

properties of Gold Nano particle :-

- It have a large surface to volume ratio.
- It have a excellent biocompatibility
- and low toxicity
- They are chemically inert.
- They have a high stability due to the gold-sulphur bonds.

Applications of Gold-Nano particles

- Detection of pathogens.
- radiotherapy dose enhancer
- phototermal agent.
- tumours detector
- Drug delivery.

Elective Course - 3 (Major)

Research methodology & current trends in chemistry

Code: 18KP3CHEL CH3

Two marks.

1. Define - Retrosynthesis
2. What is meant by supramolecular chemistry?
3. Give the structure of crown ether?
4. Give the application of crown ethers?
5. What is meant by phase transfer catalysis?

Five marks

1. Write a breif notes on monocyclic and bicyclic target moleculer?
2. What is meant by functional group interconversions? Give example?
3. Write about crown ethers?
4. Give the synthesis of 18-crown-6?

10 marks.

1. Give the application of crown ethers?
2. Write the following
   - i) diamino crown ether
   - ii) Azocrown ether,
   - iii) dibenzo-18-crown-6

Elective course - 3 (Major)

Research methodology & current trends in chemistry

Code: 18KP3CHELCH3

UNIT - 5

5. Neo synthetic methods

Retro synthetic analysis.

Retro synthetic analysis is a technique for solving Problems in the planning of organic syntheses. This is acheived by transforming a target molecule into simpler Precursor structures regardless of any potential reactivity/ interaction with reagents. Each precursor material is examined using the same method. This procedure is repeated untill simple or commercially available structure are reached. These simpler / commercially available compounds can be used to form a synthesis of the target molecule. E.J. corey Formalized this concept in his book "The logic of chemical synthesis".

Definitions.

Disconnection.

A retrosynthetic step involving the breaking of a bond to form two (or more) synthons.

Retron.

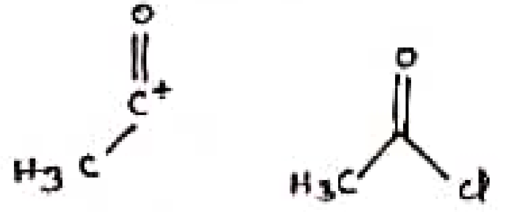
A minimal molecular substructure that enables certain transformations.

Retrosynthetic tree.

A directed acyclic graph of several (or all) possible retrosyntheses of a single target.

Synthon

A fragment of a compound that assists in the formation of a synthesis, derived from that target molecule. A synthon and the corresponding commercially available synthetic equivalent are shown below.

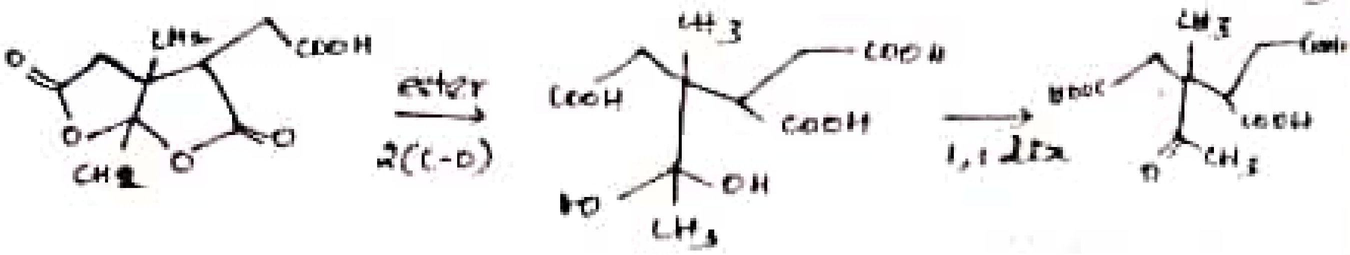


Target

The desired final compound

Transform

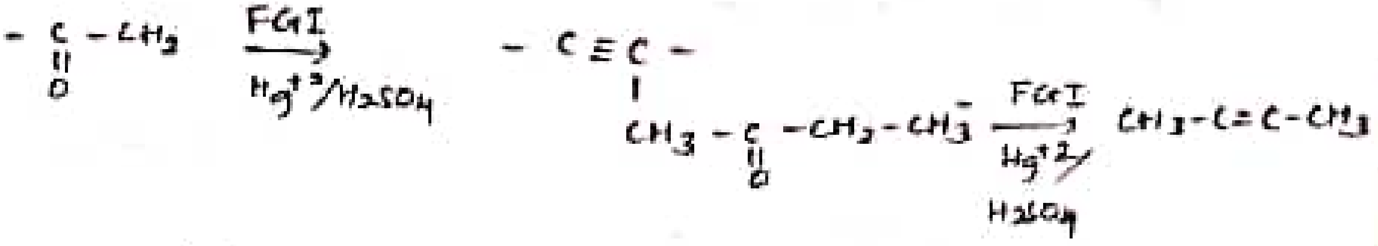
The reverse of a synthetic reaction, the formation of starting materials from a single product.



Functional group interconvertions. (FGI)

Writing of one functional group for another so that disconnection becomes possible to get the starting material available in the market.

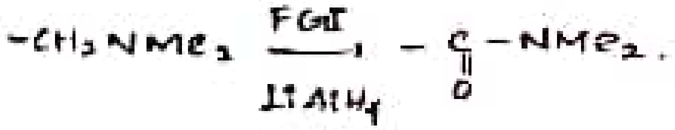
i) $-CH_2OH \xrightarrow{FGI} -CO_2Et$

ii)


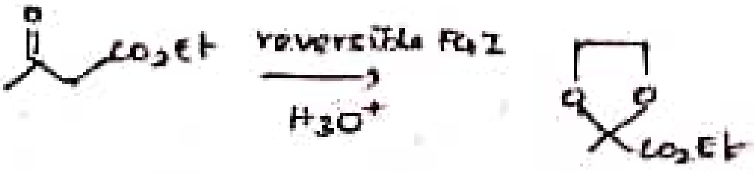
$-\underset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[Hg^{+2}/H_2SO_4]{FGI} -C\equiv C-$

$CH_3-\underset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[Hg^{+2}/H_2SO_4]{FGI} CH_3-C\equiv C-CH_3$

iii) $-COOH \xrightarrow[H_3O^{\oplus}]{FGI} -CN$

iv)


$-CH_2NMe_2 \xrightarrow[LiAlH_4]{FGI} -\underset{O}{\overset{\|}{C}}-NMe_2.$

v)


Functional group interconvertion is also necessary for functional group protection.

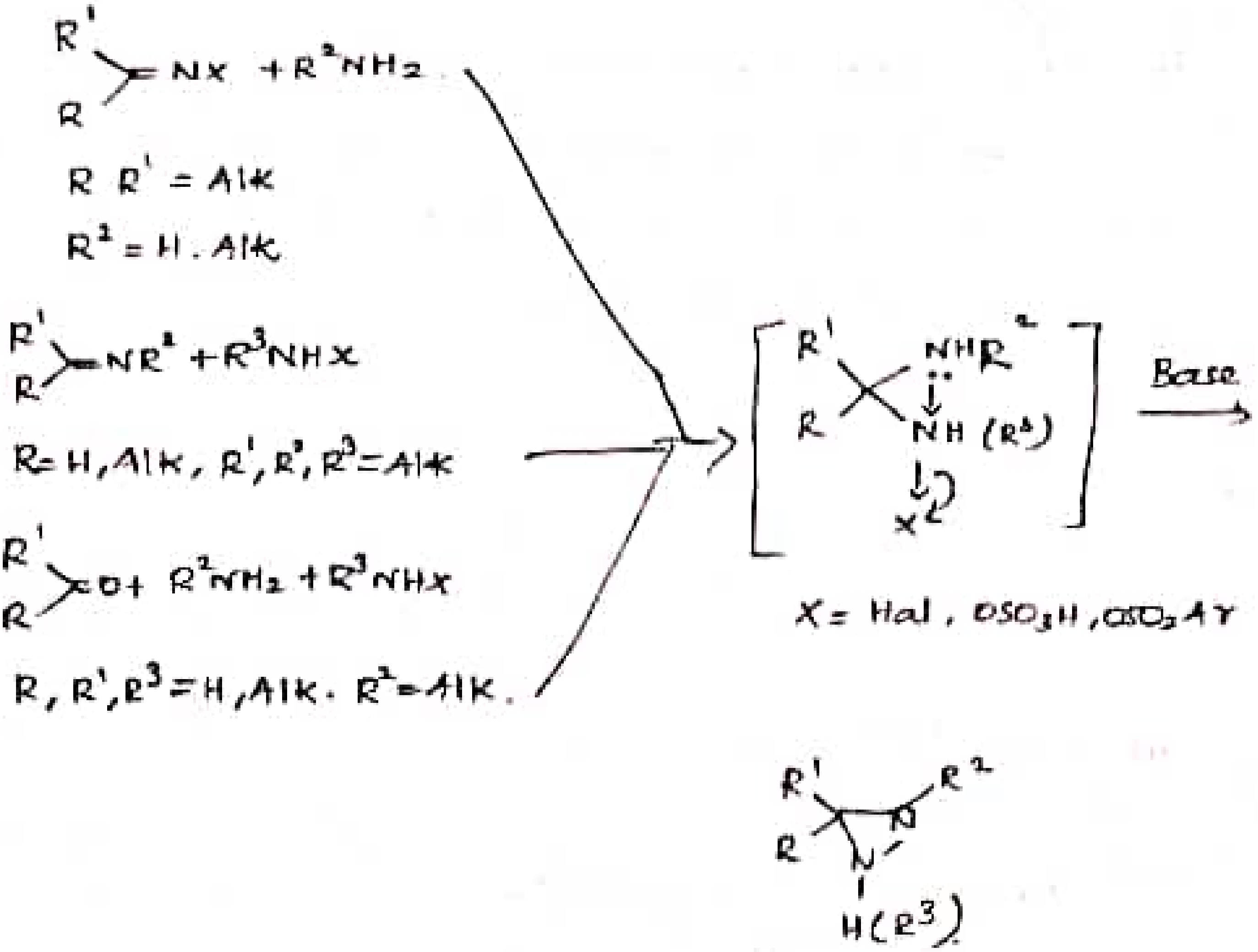
Synthesis.

Synthon (SN)

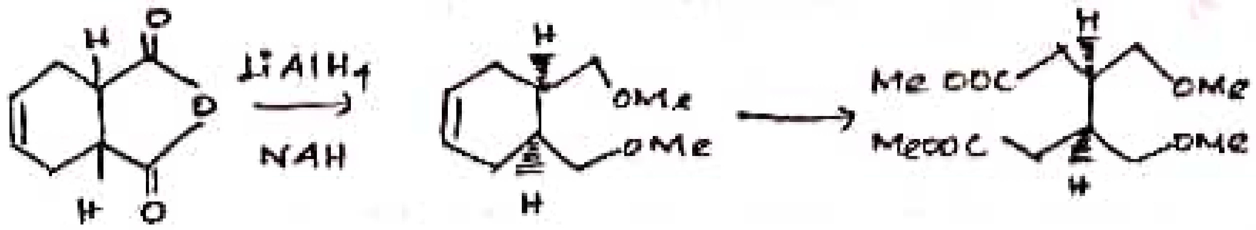
A generalized fragment, usually as ion real (or)

Retrosynthetic analysis of monocyclic & bicyclic target molecules.

Monocyclic.



Bicyclic.



Bicyclic double lactone used as precursor for all four heterocyclic ring in synthesis, disconnection of both lactones reveals a ketone.

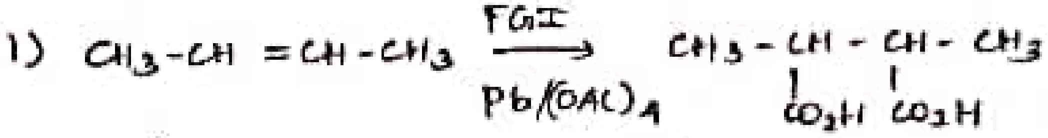
Imaginary bond cleavage may (or) may not be an intermediate in the real synthesis.

Examples.

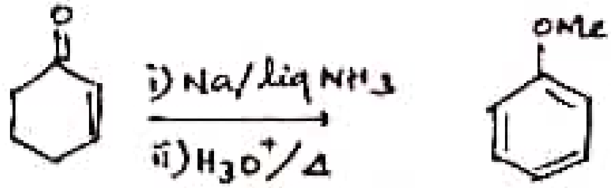
i) $CH_3 \nmid CH_2-OH \xrightarrow{dis} \underset{SN}{H_3\overset{\ominus}{C}} + \underset{SN}{CH_2OH}$

If synthon may be neutral species. Neutral synthon cannot be developed within a molecule directing but may be developed within a indirectly from other groups or molecules, which are synthesis, equivalents. Neutral synthon synthetic equivalents are actually functional group inter conversion (FGI) and or functional group addition.

Example.

1) 

$CH_3-CH=CH-CH_3 \xrightarrow[Pb(OAc)_4]{FGI} CH_3-\underset{CO_2H}{CH}-\underset{CO_2H}{CH}-CH_3$

ii) 

SE

iii) 

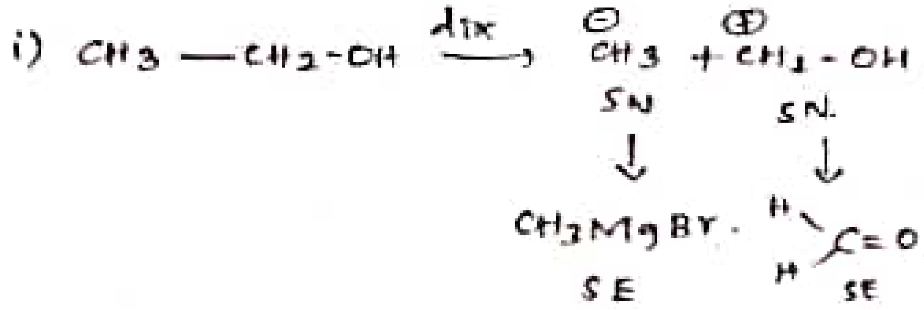
$H_3C-\underset{\overset{\|}{O}}{C}-CH_2-CH_3 \xrightarrow{FGI} H_3C-C\equiv C-CH_3.$

SE.

Sometimes neutral intermediates which are not available in the market may be considered as neutral synthons.

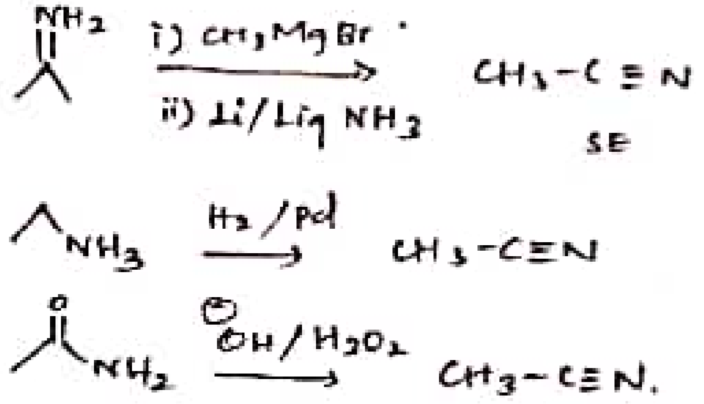
Synthetic equivalent (SE)

The actual compound Recoganizable starting material which is available in the market (or) easy to derive carrying - out the function of synthon (which is charged species usually) as it cannot itself be used because of its instability. Synthetic equivalent is a logical Precursor of target molecule.



$$\text{i)}\ CH_3-CH_2-OH \xrightarrow{dis} \underset{SN}{\overset{\ominus}{CH_3}} + \underset{SN.}{\overset{\oplus}{CH_2}}-OH$$

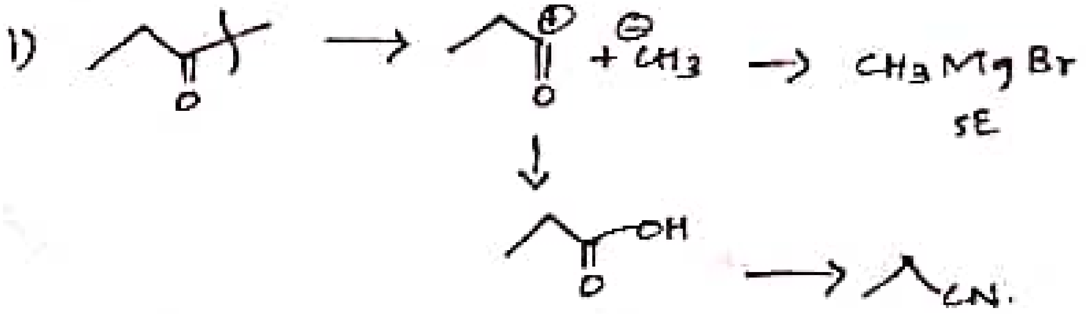
$$\underset{SE}{CH_3MgBr}.\qquad \underset{SE}{H_2C=O}$$



one - group disconnections.

Disconnection of a target molecules aiming one Particular functional group is disconnection in which involve only one functional group is the one group disconnection.

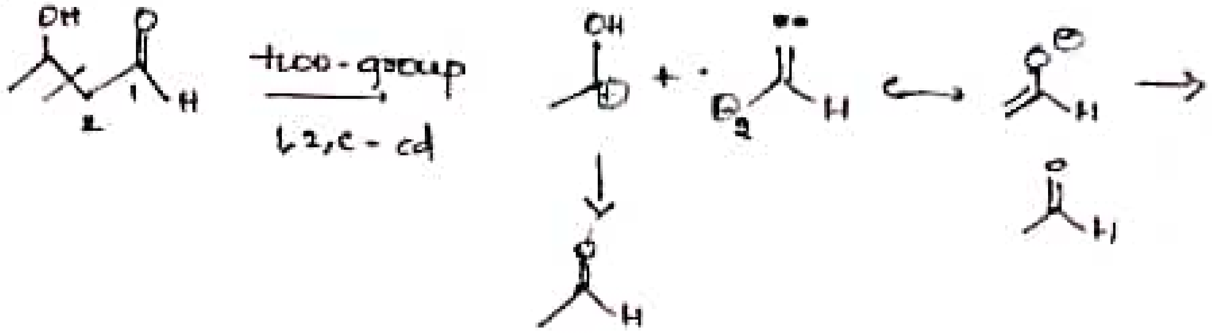
Example



Two group disconnection.

When a target molecule contain the functional group and if disconnection is done using the two together. i.e, using of one functional group to help to disconnect another is the two-group disconnection.

Example,

i) 

5.2 Supramolecular chemistry

Supramolecular chemistry refers to the area of chemistry concerning chemical systems composed of a discrete number of molecules. The strength of the forces responsible for spatial organization of the System range from weak intermolecular forces, electrostatic charge, or hydrogen bonding to strong covalent bonding, Provided that the electronic coupling strength remains Small relative to the energy parameters of the component.

Introduction

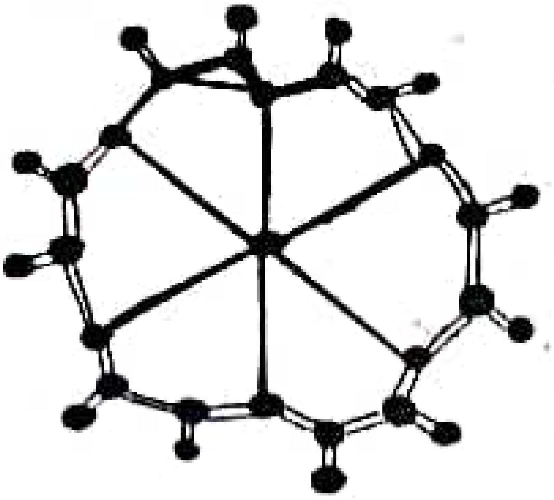
The existence of intermolecular forces was first Postulated by Johannes Diderik vander Waals in 1873. However, . Nobel laureate Hermann Emil Fischer developed supramolecular chemistry's philosophical roots. In 1894 Fischer suggested that enzyme - substrate interactions take from of a "lock and key", the fundamental Principles of molecular recognition and host - guest chemistry.

The use of these principles led tor an increasing understanding of protein structure and other biological processes. For instance, the important break through that allowed the elucidation of the double helical structure of DNA occured when it was realised that there are two seperate stands of nucleotides connected through hydrogen bonds. The use of non-covalent bonds is essential to replication because they allow the strands to be seperated and used to complete new double stranded DNA.

CROWN ETHER

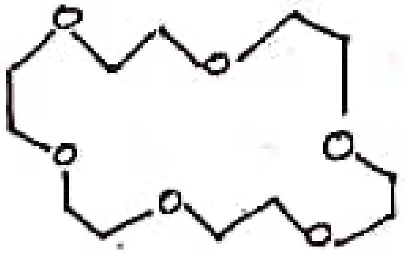
Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are cyclic oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i,e., $-CH_2CH_2O-$. Important members of this series are the tetramer (n=4), the pentamer (n=5), and the hexamer (n=6). The term "crown" refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person's head. The first number in a crown ether's name refers to the number of atoms in the cycle, and the second number refers to the number of those atoms that are oxygen.

Crown ethers are much broador than the oligomers of ethylene oxide; an important group are derived from catechol. Crown ethers strongly bind certain cations, forming complexes. The oxygen atoms are forming complexes.



SYNTHESIS OF (18) CROWN -6.

18-crown-6 is an organic compound with the formula $[C_2H_4O]_6$ and the IUPAC name of 1,4,7,10,13,16-hexaoxacyclooctadecane. It is a white, hygroscopic crystalline solid with a low melting point. Like other crown ethers, 18-crown-6 functions as a ligand for some metal cations with a particular affinity for potassium cations. The point group of 18-crown-6 is S_6. The dipole moment of 18-crown-6 varies in different solvent and under different temperature. Under 25°c, the dipolemoment of 18-crown-6 is 2.76 ± 0.06 D in cyclohexane and 2.73 ± 0.002 in benzene. The synthesis of the crown ethers led to the awarding of the Nobel prize in chemistry to charles J. Pederson.



[18-crown-6]

chemical formula : $C_{12}H_{24}O_6$

IUPAC Name : 1,4,7,10,13,16 - hexaoxacyclooctadecane

Melting point : 37 to 40°C.

Boiling point : 116°C.

Solubility in water : 75 g/L

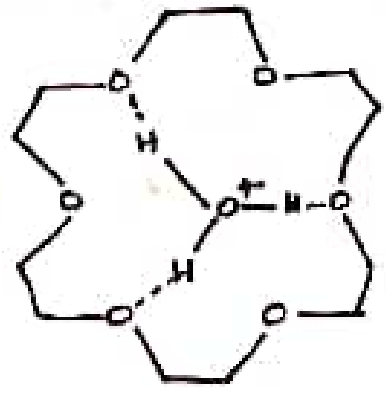
SYNTHESIS

This compound is prepared by a modified Williamson ether synthesis in the presence of a templating cation. It can be also prepared by the oligomerization of ethylene oxide.

$$(CH_2OCH_2CH_2Cl)_2 + (CH_2OCH_2CH_2OH)_2 + 2KOH \longrightarrow$$

$$(CH_2CH_2O)_6 + 2KCl + 2H_2O$$

It can be purified by distillation, where its tendency to supercool becomes evident. 18-crown-6 can also be purified by recrystallisation from hot acetonitrile. It initially forms an insoluble solvate.



18-crown-6 has a high affinity for the hydronium ion H_3O^+, as it can fit inside the crown ether.

Diamino crown ether

Dialdehydes 1 are condensed with enantiomerically pure trans-cyclohexane diamine to form the schiff base 2 followed by reduction with sodium borohydride to afford the aza crown analogues 3. The synthesis of dialdehyde ether linkers 1 has been reported previously (3,4) and involves the conversion of glycols to di-bromo ethers followed by a williamson etherification of salicylaldehyde to yield the desired precursors. We were able, through some minor modifications and application of novel microwave technology, to improve upon the overall efficiency of this preliminary process.

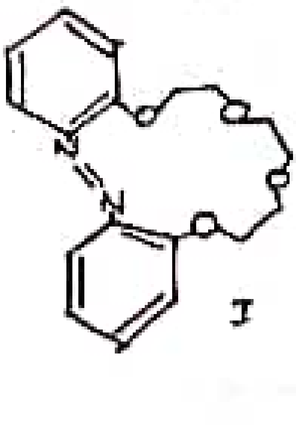
Compounds 2a and 2b could be synthesised in the absence of solvent by simply grinding the reactants, however, this neat approach was not as effective for 2c, and 2d, as dialdehydes 1c and 1d are oils at room temperature. In these instances schiff base formation was achieved in ethanolic solutions, the product seperating as an oil. Reaction times and yields for both steps are included in table 1.

compound	Time (ms)	yield (%)	compound	time (h)	yield (%)
2a	25	89	3a	4	80
2b	20	95	3b	4.5	91
2c	30	95	3c	5	92
2d	30	95	3d	5	91

AZO CROWN ETHER

Crown type polyether azo dyes 1-3 were synthesised, and the ion-pair extraction of sodium and potassium ion was studied. The extraction behaviour resembles those of benzo-type crown ethers, but changes on light lumination due to trans-cis-isomerization of the dyes. The cis-form lacks the affinity for metal ions.

The application of crown ethers in analytical chemistry is expanding rapidly. In order to meet various demands in analytical chemistry, particularly, the demand to use a crown ether structure for the alkali and alkaline earth metal-selective chromogenic reagents, a new skeletal modification of the crown ether ring is highly desirable. In this communication we would like to report on the synthesis and the metal extraction property of a new family of crown ether dyes 1,3, in which the chromophoric azo group is directly involved in the crown ether skeleton.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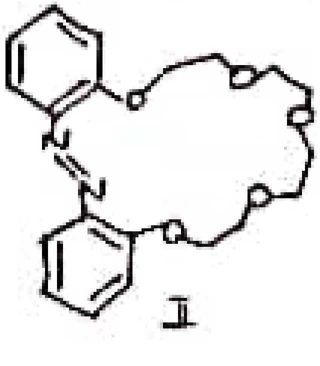
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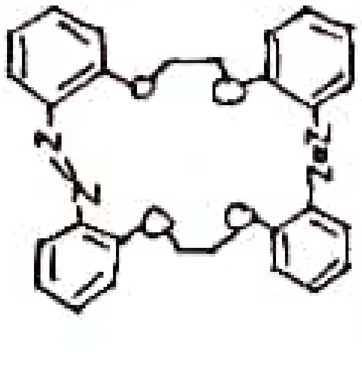
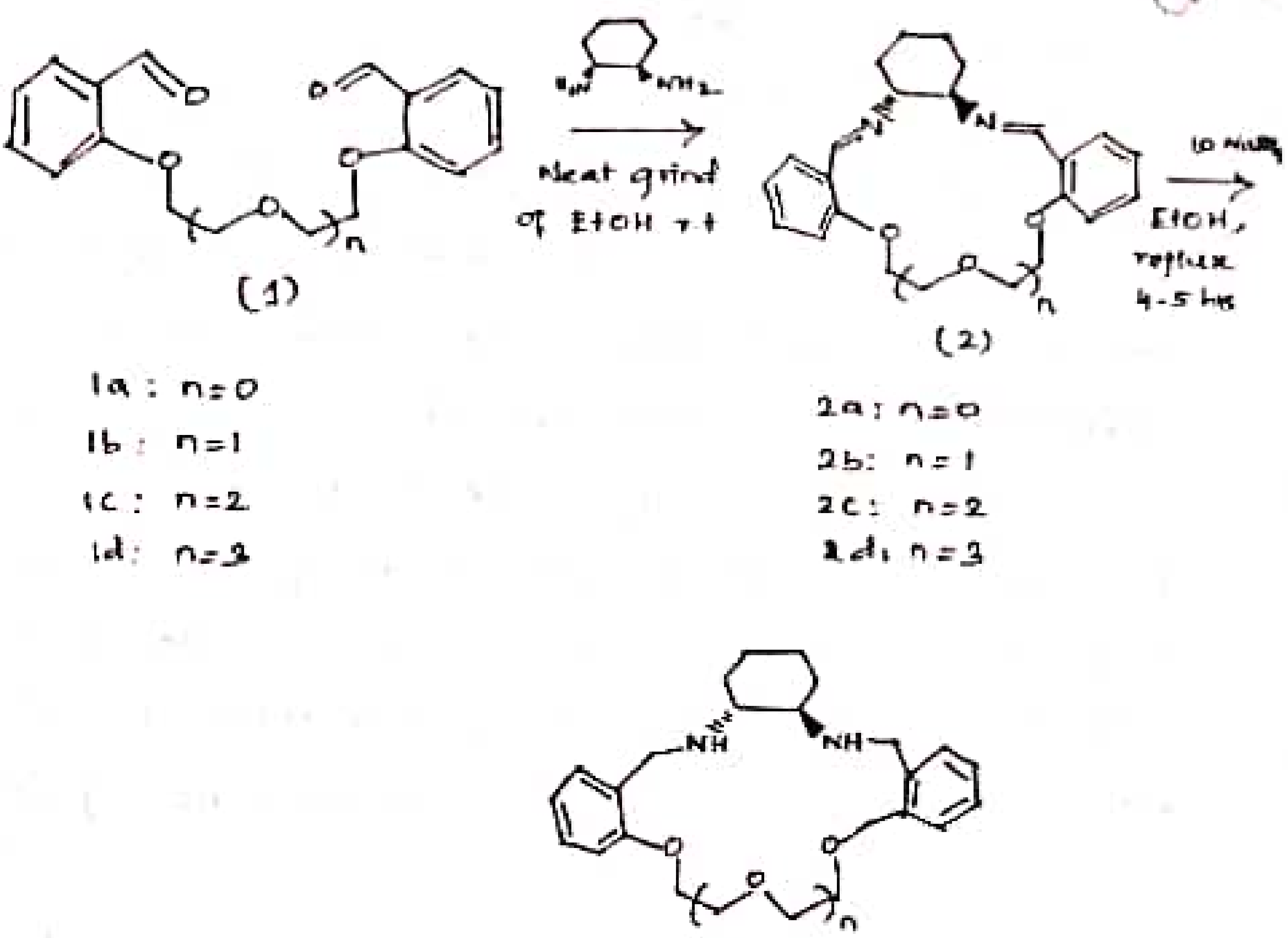

III



(1)

1a : n=0
1b : n=1
1c : n=2
1d : n=3

(2)

2a : n=0
2b : n=1
2c : n=2
2d : n=3

(3)

3a : n=0
3b : n=1
3c : n=2
3d : n=3

In most cases the reduced macrocyclic products 3 were isolated as oils. Subsequent purification involved the precipitation of hydrochloride in salts by reaction with excess hydrochloride in ether. The ^{1}H, and ^{13}C-NMR spectra of the respective schiff bases 2 and diamino products 3 were consistent with the assigned structures in all case. There was no spectroscopic evidence for the presence of any imine protons once the reduction had been performed.

The dyes 1-3 were synthesized by the reaction of 2,2'-dihydroxyazobenzene with the appropriate oligoethyl-eneglycol dichloride or ditosylate in the presence of a calculated amount of potassium t-butoxide in dry THF. In a typican run, the dye I was prepared in the following procedure. Tri-ethyleneglycol ditosylate (3.2 g, 1.4×10^{-2} mol, in 100 ml THF was added dropwise in 1 h to a solution of potassium t-butoxide (3.2 g, 2.8×10^{-2} mol) and 2,2'-dihydroxyazobenzene (3.0 g, 1.4×10^{-2} mol) in 100 ml dry THF, and the mixture was refluxed for 20 h, with vigorous stirring under nitrogen. After filtering the precipitates, the filtrate was concentrated to obtain the residue, which was taken in chloroform, washed with water, and finally recrystallized from heptane. These are reddish orange crystals, soluble in common organic solvents and insoluble in water. The elemental and instrumental analysis fully supported the proposed structures -4.

Alkali metal ions were extracted from aqueous solution into benzene using the azo-crown ethers and tetrabromophenolphthalein ethyl ester ($TBPE^{+}$) as a pairing anion at pH 9. The extraction constants $K_{ex} = \dfrac{[H^{+}\cdot \text{crown}\,\text{TBPE}^{\pm}]_{org}}{[M^{+}]\,[\text{crown}]_{org}\,[\text{TBPE}^{\pm}]}$

for Na^+ and K^+ are summarised in table 1.

Extraction constants of crown ethers.

		log Kex.	
M^+	1	2	D618C6
Na^+	4.18	4.01	3.84
K^+	2.77	5.01	5.69

APPLICATION OF CROWN ETHERS.

Synthetic applications.

Esterification,
Saponification,
anhydride formation
Potassium permanganate oxidation
Aromatic substitution reactions
Elimination reactions
Displacement reaction
Generation of carbenes
superoxide anion
Alkylations - i) o-alkylations
ii) c-alkylations
iii) n-alkylations.

Analytical application.

Determination of gold in geological samples.

Super critical fluid extraction of trace metal from solid and liquid materials.

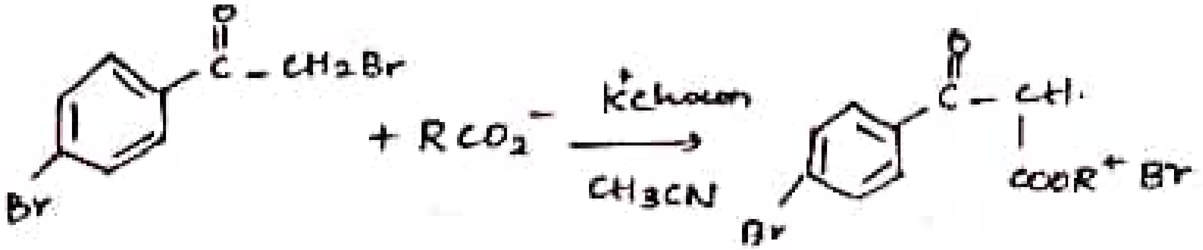
Application of ionic liquids in analytical chemistry oxidation and determination of aldehydes

Crown ethers are used in the laboratory as phase transfer catalyst.

Esterification.

Crown ethers have been used for esterification. P-bromo Phenacyl esters have been prepared by the reaction of P-bromophenacyl bromide with potassium salt of carboxylic acid using 18-crown-6 as the solubilizing agent, which yields 92% phenacyl esters of fatty acids are obtained.

R = H, CH_3



Uses of crown ethers.

Complexes between crown ethers and ionic salts are Soluble in nonpolar organic solvents, creates reagents that are free or water that have useful properties. Inorganic salts dissolve in organic solvents leaving the anion unassociated, enhancing reactivity.

Phase transfer catalyst (PTC)

In a chemistry, a phase-transfer catalyst or PTC is a catalyst that facilitates the migration of a reactant from one phase into another phase where reaction occurs. Phase-transfer catalysis is a special form of heterogeneous catalysis is a special form of heterogenous catalysis. Ionic reactants are often soluble in an aqueous phase but insoluble in an organic phase in the absence of the phase-transfer catalyst. The catalyst functions like a detergent for solubilizing the salts into the organic phase. Phase-transfer catalysis refers to the acceleration of the reaction upon the addition of the phase-transfer catalyst.

By using a PTC process, one can achieve faster reactions, obtain higher conversions or yields, make fewer by products, eliminate the need for expensive or dangerous solvents that will disolve all the reactants in one phase, eliminate the need for expensive raw materials and/or minimize waste problems.

Applications

PTC is widely exploited industrially. Polyesters for example are prepared from acyl chlorides and Bisphenol-A. Phosphothioate-based pesticides are generated by PTC-catalyzed alkylation of phosphothioates. One of the more complex applications of PTC involves asymmetric alkylations, which are catalyzed by chiral quaternary ammonium salts derived from cinchona alkaloids.

CATENANES

A catanene is a mechanically - interlocked molecular architecture consisting of two or more interlocked macrocycles, i.e., a molecule containing two or more intertwined rings. The interlocked rings cannot be seperated without breaking the covalent bonds of the macrocycles. catenane is derived from the Latin catena meaning "chain". They are conceptually related to other mechanically interlocked molecular architectures, such as rotaxanes, molecular knots or molecular Borromean rings. Recently the ~~Knots or molecular~~ terminology "mechanical bond" has been coined that describes the connection between the macrocycles of a catenane. Catenanes have been synthesised in two different ways; statistical synthesis and template-directed synthesis

Synthesis

There are two primary approaches to the organic synthesis of catenanes. The first is to simply perform a ring- closing reaction with the hope that some of the rings will form around other rings giving the desired catenane product. This so called "statistical approach" led to the first successful synthesis of a catenane, however, the method is highly inefficient, requiring high dilution of the 'closing' ring and a large excess of the preformed ring, and is rarely used.

The second approach relies on supramolecular preorganization of the macrocyclic precursors utilizing hydrogen bonding, mental coordination, hydrophobic effect or coloumbic interactions. These non-covalent interactions offset some of the entropic cost of association and help position the components to form the desired catenane upon the final ring-closing. This "template directed" approach, together with the use of high pressure conditions, can provide yields of over 90%, thus improving the potential of catenanes for applications. An example of this approach used bis-bipyridinium salts which form strong complexes threaded through crown ether bis-34-crown-10.