HALOALKANES AND HALOARENES

(ORGANIC CHAPTER-1)

Topic-1:- Classification

(a) en the basis of number of halogen atem:

CH5X

CH2X

CH2X

CH2X CHX

CHOX

R-X An alkyl halide IUPAC-haloalkane

R-Ackyl or substituted

X-F,U,Br,I

Monohaloalkane

Dihaloalkane

Trihaloalkane

AY-X An Any halide

IUPAC-haloarene

Ar-phenyler.

Enbstituted phenyl X-F,U,BY,I

Dinawarene

Tribalogrene

Monohaloarene

The dihalo-compounds having the same type of halogen atom are further classified as:-

(à) Gem-dihalide: In these desivative, both the halegen atom are attached to the same canbon atom.

H + - c - c - u

Common name: Ethylidene chleride

IUPAC name: - 1,1-Dichloroethane

(b) wir-dihalide - In these derivative, both the halogen atom are attached to adjacent (vicinal) carbon atem.

eg: - u - CH2 - CH2 - Cl Common-name: - Ethylene dichloride

· MICKLES INC.

IUPAC name: - 1,2-Dichlowoethane

(1,2-Dichloroethane)

- Gem-dihalide are also known as alkyridene halide
 - Vri déhalide are also known as alkylene halide.

ALKALIES AND EIALONKENIES (b) compounds containing C-X band, where carbon is ep3 hybridised (i) Alkyl halide or Halvalkane: The functional group is attached to the caubon, that carbon is directly attached to new many carbon. If 0 or 1-1° Eg: - CH3-CH2-CH2-CL:-(1°) CH3-CH-CH3:- (2°) Int dietum a CH2 CH3-c-CH3:-(3°) (ii) Allylie Halide: The halogen atom is attached to the ep3 hybridised cauben atom which is adjacent to denble bond. CH = CH - CH2 CH2 = CH - CH2 - I Eg :-3-Chlerocyclohex-1-ene 3-Iodoprop-1-ene 3-Chlero-1-phenylprop-1-ene (iii) Benxylie Halide: In these halide, the halogen atom is bended to a cps hybridized causon atom which is next to the benzene ring. Eg:- CH2X Benzyl Halide Draikyrbenzyl halide (C) compounds containing C-X band, where coupon is sp2 hybridised (2) Vinytre Halide: - In these halide, the halegen is bended to caubencausen double bend which is ep2 hybridised 9:- CH2= CH-X Vinyl halide 1-Halocyclohex-1-ene (ii) Aryl Haride: In these haride, the halegen atem is directly attached to ep2 hybridised caubon atom of the accomatic ring. Halobenzene

Nomenclature

IUPAC names of some halides that were asked in beaud enamination:

The transmission of the second of the second

STRUCTURE	IUPAC name	STRUCTURE	IUPAC name
1. CH3 = CH3	4-Bramo-3-methyl-pent-	10. UN02	2,4- Introchioro benzene
th ch3 By	2-ene.	4	(2,4-Dinitrochlorobenzene)
2.	1.15	N02	
CH3- CH-CH2-CH-CH3	2-Bromo-4-chloropentane	11. CHg	
br a	n de la companya de l	CH3-C-CH2CL	1-chloro-2,2 dimethyl propane
3.			
CH3-CH-CH2-CH= CH2	4-chipropent-1-ene	12.	
i a		(CH3)2CH·CH(U)CH3	2-chloro-3-methyl butane
4. Q CH3	2,5-Dichlarotoulene/	13.	
a all	1,4-Dichloro-2-methyl benzene	CH3-CH-CH2-CH-CH3	2-Bramo-4-chlaro
5.		o a	pentane
CH3-C= C-CH20+1	2-Brama-2-mathild	13.	
CH3 BV	2-Bramo-3-methylbut- 2-en-1-al	CH2=CH-CH2-CL	2-chinungs
CH2U		By	3-chionoprop-1-ene
6. CH2U	Phenylchloromethane	15. De	1,3-Dibromobenzene
7. (CH3)3 CGH2BY	1-Bromo-2,2-dimethyl propane	16. O BA	3-Bramotaulene
head	prapane	BY	S Wishingtone
8. CH3 H	was a see that one	TE MULTINET FRANCE	Six and of the figure
)=(H	4-Bromopent-2-ene	7: CHC13	Inchloromethane
H / 1 } Bx			estimate and the
HgE		Br	
9. H CH3	10000	18. CH3- C-CH3	2,2-Dibromopropane
J H Q 4	1-ene	Br	ropule
Hac			
9			111111111111111111111111111111111111111

Topic-3

METHODS OF PREPARATION OF HALDALKANES AND HALDARENES:

and first seather hatequivilen flow such as anothern

1 FROM ALCOHOLS:-

(a)
$$R-DH + HU \xrightarrow{XnU_2} R-U+H_2O$$

Eq: $CH_3-OH + HU \xrightarrow{XnU_2} CH_3-U+H_2O$

: Eg: - CH3CH2OH + NaBr+ H2SO4 -> CH3CH2Br+ NaHSO4+ H2O (c) 3R-OH + PX3 - 3R-X + H3PO3 (X=U, Bx) Eg: - 3 C2+15 DH + PU3 -> 3 C2+15 C1 + H3 PO3 Ethanol Chloroethane Phospherous aid (d) R-OH + PUS --- R-U + POUZ + HU <u>Eg:-</u> CH3 CH2 CH20H + PUS - CH3 CH2 CH2 CH2 CH + POUZ + HCL Puppanol Chloropoppane Phosphorous oxychloride $\frac{\operatorname{red} P/X_2}{(X_2 = Bx_2, I_2)} R-X$ Eq: - CH3-OH red P/ BY2 CH3-BY (f) R-OH + SOU2 --- R-a + SO2 + Ha > C2H5U+SO2+HU Eg: - C2H50H + SOC12 -Ethanol Thionyl chloro ethane chlouide Preparation of chloroalkane from alrohol by using thionyl chloride is the best method because the by products are gases which can be eacily removed from the reaction mixture leaving behind pure alkyl halide. Order of martinity of alcohols with a given halvaid is (2) FROM HYDROCARBONS (a) Fuce radical halogenation/free radical substitution CH3- CH2- CH3 - CH2 → CH3-CH2-CH2-CH CH3-CH-CH3 Chloropuopane 2-Chloropropane (minor) (major) Since, 2° free radical is more stable, so 2-Chloropropane is the major product.

- The autho and para isomers can easily exparated due to their large difference in melting point.
- Iodo-derivatine cannot be obtained by direct reaction with cedine as the martion is menercible.
- Flue compounds cannot be prepared by this method due to high reactivity of fluorine.

(C) SANDMEYER'S REACTION:

NH2

NaN02+HX

$$(0^{\circ}-5^{\circ}C)$$
 $(X=U,By)$

(a) (Anitine to Chloubenzene)
$$\begin{array}{c}
NH_2 \\
\hline
NaN0_2 + Hu \\
\hline
(0^\circ - 5^\circ c)
\end{array}$$

$$\begin{array}{c}
V_2 \overline{u} \\
\hline
cv_2 u_2
\end{array}$$

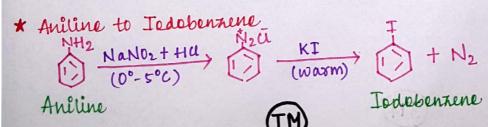
$$\begin{array}{c}
U \\
\end{array}$$

$$\begin{array}{c}
U \\
\end{array}$$

Aniline Benrene diazonium Chlorobenzene Chronide

Aniline

When aniline is treated with NaNO2 and HU at (0°-5°C) it founds benxene diazonium chloride from which chlorobenzene is prepared by reacting with Cuille and bromobenhere is prepared by reacting with Cu2B72.



(d) FROM ALKENES

(i) Addition of hydrogen halides:

(ii) Adaition of halogens:-

$$C = C + + Bv_2 - CU_4 \rightarrow Bv_2 - CH_2 - CH_2 Bv_3$$

(C) HALOGEN EXCHANGE

(2) Finkelstein neartion

$$\frac{Eq:-}{R-X+NaI} \xrightarrow{dry} \frac{dry}{avetone} \xrightarrow{R-I+NaX} (X=U,Bx)$$

$$\frac{Eq:-}{R-U+NaI} \xrightarrow{dry} \frac{dry}{avetone} \xrightarrow{CH_3-U+NaI} \xrightarrow{dry} CH_3I+NaU$$

$$\frac{dry}{avetone} \xrightarrow{CH_3-Bx+NaI} \xrightarrow{dry} CH_3I+NaBx$$

when askyl chlouide on askyl bromide is theated with NaI in presence of dry aretone, askyl iodide is prepared.

in Smarts reaction

$$\begin{array}{c} \text{CH}_3\text{-B} \times & \frac{\text{AgF}/\text{Hg}_2\text{F}_2}{\text{CoF}_2/\text{SbF}_3} \times \text{AgB} \times + \text{CH}_3\text{F} \\ \text{CH}_3\text{-CL} & \frac{\text{AgF}/\text{Hg}_2\text{F}_2}{\text{CoF}_2/\text{SbF}_3} \times \text{AgCL} + \text{CH}_3\text{F} \\ \end{array}$$

PHYSICAL PROPERTIES



Alkyl halides though pelan, are immissible with water because they are not able to foun hydrogen bends with water molecule.

2. DENSITY

The density inwases with inverse in number of caubon atoms, halogen atoms and atomic mass of halogen atom.

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- · Halvalkanes have higher boiling point as compared to these of corresponding alkanes because this is due to their polarity and etrong dipole-dipole interaction between harvalkane molecules.
- (i) For the same alkyl group, bp of halvalkanes decreases in the order RI>RB+>RU. This is because with increase in size and mass of halogen atom, the magnitude of vanderway force of attraction Ases.
- CH3I, CH3B8, CH3U, CH3F

Ans: - CH3I > CH3BX > CH3U > CH3F

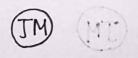
(bp=beiling peint)

- invease in the size of alkyl group. halvalkanes invease with
- 1: Arrange there C2H5U, C3H7U, C4H9U, CH3U in invuaing order of 6p.
- (iii) For isomeric halvalkanes, the bp devicase with branching ie 1° 72° 73° because the branching of the chain makes the molecule more compact and therefore decreases the surface area of halvalkanes and so the magnitude of the nander wall's force of attraction decreases.
- Q:- Annange these tent-Butyl bromide, n-Butyl bromide, Teabutyl bromide in decreasing order of their beiling point.
- An: n-Butylbremide > Irobutylbremide > text-Butylbremide.
- Q:- Arrange CH3Br, CHBr3, CH3U, CH2Br2 in invuaieng ouder at boiling

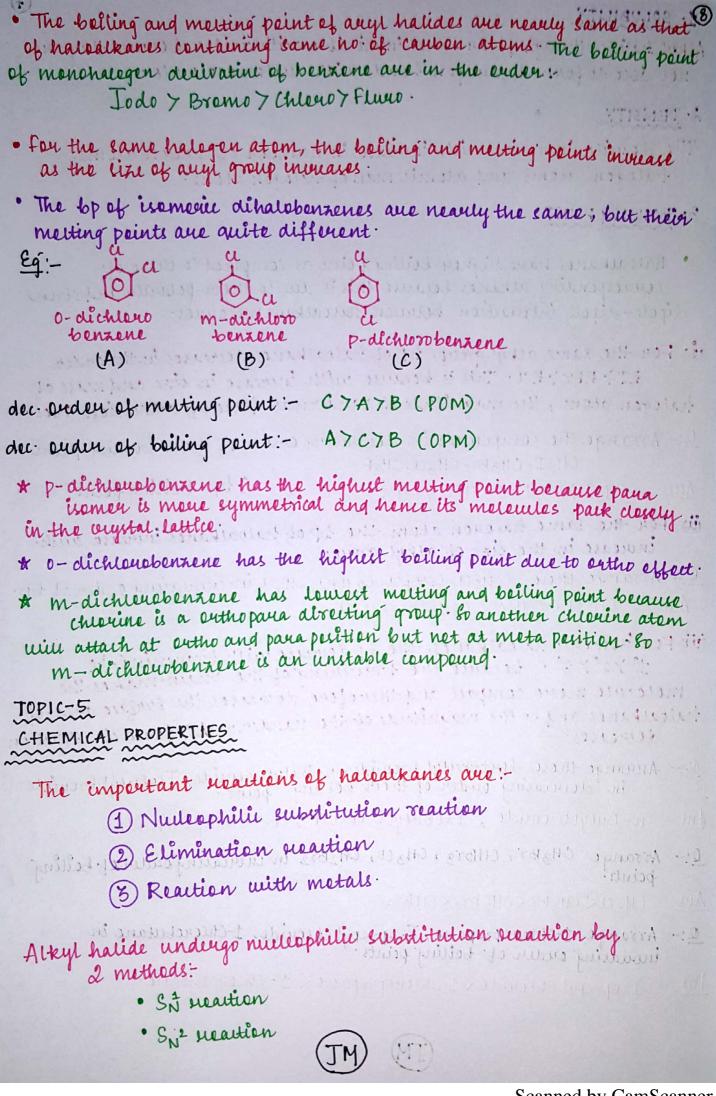
AM: CH3U< CH3BV< CH2BV2< CHBV3

Q:- Arrange 1-Chlouppopane, Isopropyl chrouide, 1-Chronobutane in inmaring order of beiling points.

Ans: - Isopropyl chlouide < 1-chloropropane < 1-chlorobutane.



washing y si



(1) Nucleophilie substitution unimolecular Nucleophilie substitution bimolecular reaction.

2) Order-1, Molecularity-2

(3) R-U+NW -> R-NU+UT Rate = K[R-U] [Nu]0

4) Rate of neartion depends on the cone. of alkyl halide and not on nuleophile. 80, unimolecular.

5) It has 2 step mechanism: 1st: - Genisation of molecule and formation of carbocation

2nd: - attack of nucleophile

6 Nuleophile will attack both at front side and backride (the front side and back side attack of nucleophile is possible due to sp2 hybridisation and planar structure of caubocation)

(7) No transition state complex is found.

8 order of reactivity is based on the Stability of carbocation; Order is 3°72°71°

(9) Due to funtise attack and backside attack metention product and innerion puraut are obtained.

SN1 is followed by Racenisation.

madian.

Order-2, Moleularity-2

R-a+ Na -> R-Nu+a Rate = k [R-U] [N@] 1

Rate of reaction depends on the cone of alkyl halide and on nucleophile. 80, biniolecular.

The approaching of nucleophile and uclease of it will center simultaneously. Hence, it is a single step mechanism.

Nucleophile will attack only at the backside because in puimary alkyl halide, there is less alkyl group and less steric hinderance.

Teranition state complex is found.

More buskies is the group, the backside appreain is hindered Hence, the order of neartivity is 10720730

Due to only backeide attack of nucleophile, innersion product is ostained.

Innersion of configuration takes place.

MECHANISM OF SN1:-

Step-1: - Louisation of molecule. CH3-C-U -> CH3-C+ U (Slew)

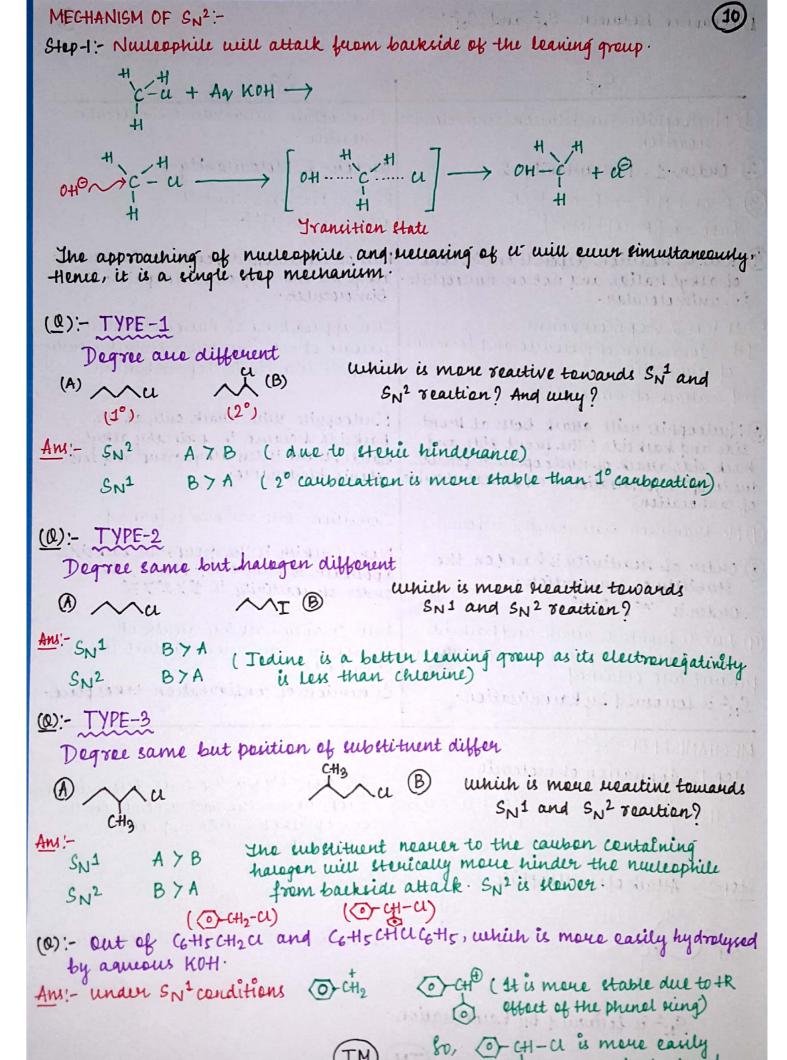
As slow step is the nate determining step, here the nate depends on the cone of alkyl halide and not on nucleophile

and some interestion

Step-2: Attack of nucleophile

OH - C (Invension) +

SN1 is followed by Racemisation.



hydrolysid.

The nucleophile which is capable of attacking the molecule therough more than one site is called as ambident nucleophile

eg:- nitrite ion, cyanide ion

Some important nucleophilie reagents:

- · NaOH (aa) -> OH (nulcophile)
- · KOH (aa) -> OHO (nucleaphile)
- · KCN (ale) → EN (nucleophile)
 Causen is the attacking atom

· AgCN(ale) -> NC (nucleophile)
Nitrogen is the attacking atom.

(1): Hawalkanes heart with KCN to form alkyl cyanides as the main purduet while Ag-CN forms isocyanides as the chief product Explain

Ans: - KCN is puedominantly ionic 80, both C and N atom over free to donate electron pair. Since, c-c bond is more stable than c-N bond, therefore attack mainly occurs through causen atom forming ackylchalide as the main product.

AgeN is mostly covalent in nature. Only Natom is free to donate electron pair and attack mostly occurs through nitrogen atom forming isocyanide as the chief product.

STERIOCHEMICAL ASPECTS OF NUCLEOPHILIC SUBSTITUTION REACTION:

1 CHIRALITY CENTRE: A causen atom which is bended to four different atoms or groups in the melewile is called chiral carbon or an asymmetric causen atom.

Latin aird (Chinal) optically action Propan-2-of (Actival) Optically inactine

2 CHIRAL OBJECT: The one that is not superimposable on its niveror image

Mimer
P A A

Chinal
(non-superimposable)

Adhiral
(superimposable)

(3) <u>ENANTIOMERS:</u> Compounds which are niver images of each other and are not superimposable.

(4) RACEMIC MIXTURE: The process of convension of one enantioneer on (12) optically active compound into a racemic mixture is called racemization. An equimolari minture of a pair of enantioners is called racemir mixture.

(5) INVERSION, RETENTION, RACEMIZATION:

C2+15

H
$$\stackrel{C}{\longrightarrow}$$

C4+15

C2+15

C2

· If (A) is the only compound obtained, the process is called Retention.

· If (B) is the only compound obtained, the process is called Inversion

· If a 50:50 (equal) mixture of A and B is obtained, the process is Racemization.

(Q):- Give Reasons:

(i) Racemic mixture is optically inactive.

Ans: A racemic minture is optically inactine as it is a mixture containing two enantioners in equal proportion and have zero optical rotation.

ii) uny is butan-1-el eptically inactine but butan-2-el is eptically active?

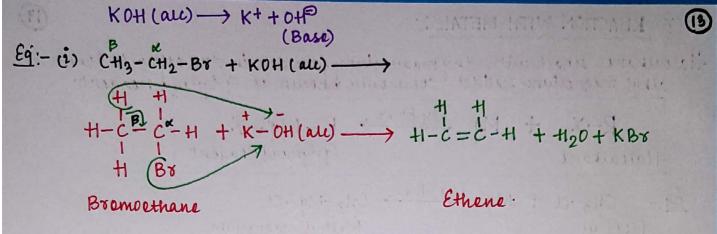
Ans: butan-1-of is optically inactine due to the absence of chinal carbon atom butan-2-of is optically actine due to the presence of Chival caubon atom.

(iii) (±) 2-Butanol is optically inactine

Ans: (1) 2-Butanol is a racemic mixture i.e. thouse are two enantiamens in equal proportions. The notation by one enantiamen will be cancelled by the netation due to other isomer, making the mixture optically inactine.

2) ELIMINATION REACTION

when a halcalkane having atteast one B-hydrogen atom is treated with (all) KOH, then there is elimination of hydrogen from the B-carbon atom and halogen from the x-carbon atom. As a result, we get alkene as the product Since, B-hydrogen atom is involved in elimination, It is also called as B-elimination.



ii)
$$CH_3-CH_2-CI+KOH(alc) \longrightarrow CH_2=CH_2+KCI+H_2O$$

Chlouaethane Ethene

In the dehydrechalogenation of 2° and 3° halpalkanes, when there is a possibility of formation of 2 arkene (one major and one minor), there we apply Saytzeff's rule or xeff sayt's rule.

SAYTZEFF'S RULE OR ZEFFSAYT'S RULE:

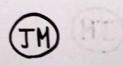
If there is a possibility of foundation of 2 alkene then the more substituted alkene is more stable.

$$\frac{\text{Eq:-(i)}}{\text{CH}_3-\text{CH}_2-\text{CH}} \xrightarrow{\text{CH}_3} \xrightarrow{\text{KOH}} \xrightarrow{\text{CH}_3-\text{CH}_2-\text{CH}_3+\text{CH}_3-\text{CH}_2$$

(a):- The treatment of alkyl chlorides with agreeus KOH leads to formation of alcohols but in presence of alcoholic KOH, alkenes are the major products. Emplain.

Ans: In aqueous solution, KOH is almost completely ionized to give OH ions. These being strong nucleophius result into substitution reaction on ackyl hariae to form alcohols. At the same time in aqueous solution, the OH ions are highly hydrated. This hydration reduces the basic character of OH ions which, therefore, fails to abstract a proton (H+) from the \beta-carbon atom of alkey chloride to form an alkene.

An contract, an alcoholic exterior of KOH contains alkoxide (Rō) ions which being a stronger base than OH ions preferentially eliminates a molecule of HCl from an alkyl chloride to four an alkene.



3 REACTION WITH METALS:

(1)

Halvalkanes react with dry magnesium pourder in dry extrer to form alkyl magnesium halides commonly known as Gregnand neagent.

WURTZ REACTION :-

when & same asky halide steast with metallic Na in presence of dry other we get higher askanes containing double the number of caubon atoms present in the haloarkane.

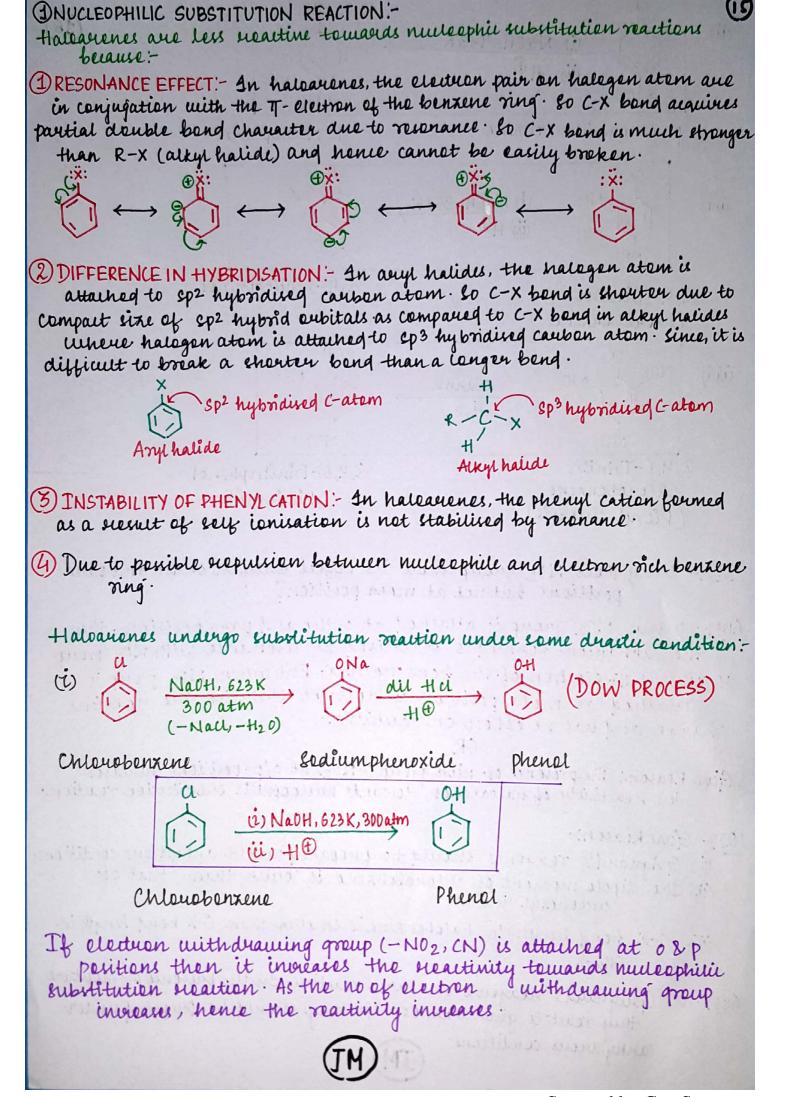
* Only 1° and 2° natoalkanes undergo Wurtz eleaction while 3° haloalkanes prefer to undergo denyderonalegenation to four alkenes.

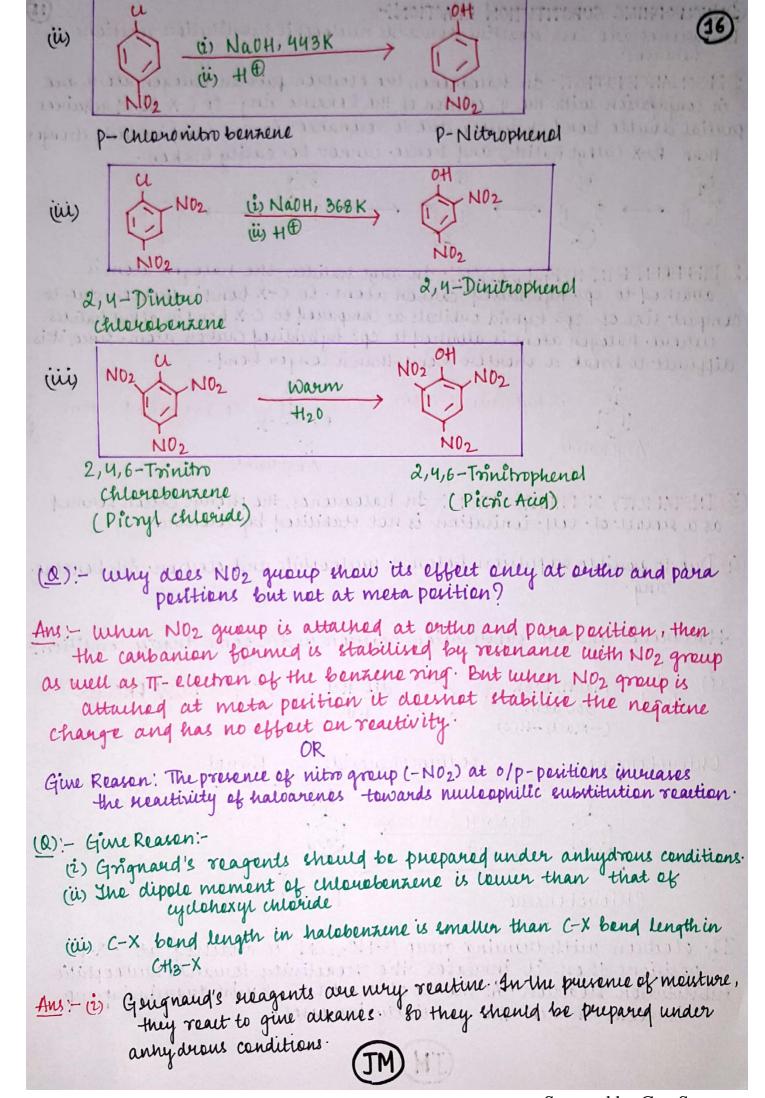
TOPIC-6

REACTION OF HALDARENES:-

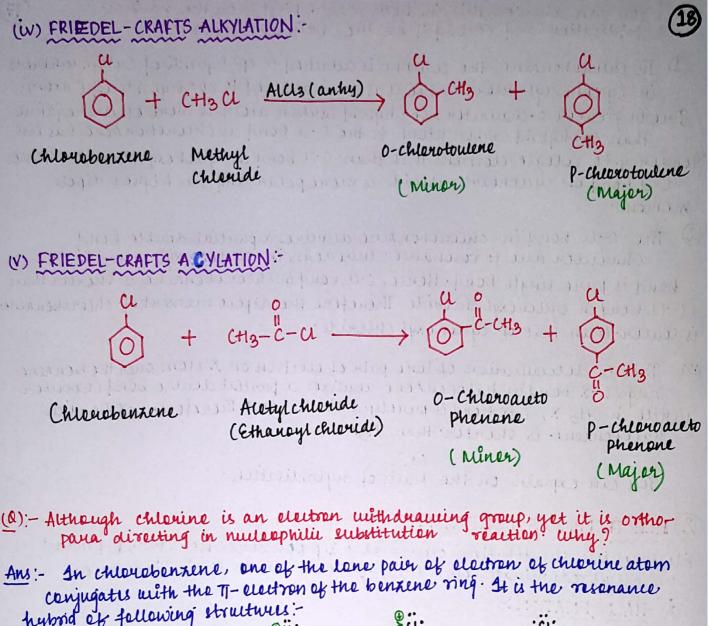
- 1) NUCLEOPHILIC SUBSTITUTION
- 2 ELECTROPHILIC SUBSTITUTION
- 3 REACTION WITH METALS







hybridisation and second is on the basis of resonance] (1) In chlouobenzene, the cratom is attached to ep2 hybridised Catom whereas
in cyclone my chloride, the clatem is attached to ep3 hybridized catem. Due to greater s-character, sp2 hybrid carbon atom is more electronegative than sp3 hybrid carbon atom. so the C-cl bond in chlorobentene has less tendency to release electrons to cl than C-cl bend in cyclonexyl chloride. Hence, C-cl bond of cyclonexyl chloride is more polar and has higher dipole moment.
2) The C-U bond in chlouobonxene acquires a partial double bond character due to resonance whereas, in cyclopexyl chloride C-Ce bond is pure single bond. Hence, C-U bond in Chlouobonnene is shorter than C-Cl bond in cyclopexyl (filogide: Therefore the dipole moment of chloride: Therefore the dipole moment of chloride.
C-CI band in cyclonexyl Chloride. Therefore the dipole moment of chlorobennine is conser than that of cyclonexyl Chloride.
iii) Due to delocation of lone pair of electron on X atom over the benzene ring, c-x bond in halobenzene acquires a partial double bond character unite in CH3-X, c-x bond is purely a single bond. Therefore c-x bond in halobenzene is thorten than CH3X
You can explain on the basis of hybridisation.
2 ELECTROPHILIC SUBSTITUTION:
Electrophilic substitution accurs at 0 & p positions. However, p-product usually predominates over the o-product due to eteric hindrance. (i) HALOGENATION: a Anny Fells a O-Dichlorobenzene
Chlorobenzene P-Pichlorobenzene (Minor)
the cheese them for a political as electronices are madic substitutions of the substitutions
HN03 NO2 + CO CANADANA
Conc. H2 504 OT 1002 + O
Chlouobenzene 0-Chlouonitro NO2 p-Chlouonitrobenzene bonzene (Major)
üis SULPHONATION:
cone. H2504 + O P-chlorobenzene
Chlorobenzene 0-Chlorobenzene so3H sulmanie acid (minor) culphonic acid (minor)
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hybrid of following structures:

Since, electron density is maximum at ortho and para positions due to + Reffect, therefore an electrophile can easily attack at such positions. Hence, chloudbenzene is 0,p-directing in electrophilic arematic substitution reactions.

(3) REACTIONS WITH METALS:

(i) FITTIG REACTION: When two same ary halides react with Na in puesance of dry ether, we get two ary groups which are joined together

JAKELLINE !

(") WURTZ-FITTIG REACTION:

(19

when arky halide nearts with anyl halide in presence of sadium and dry other, then we get arky benzene

(a):- DEFINE INVERSION AND RETENTION.

Ans: - Inversion: If the preduct formed in a reaction has a etereochemistry opposite to that of reactant, it reads to inversion of configuration

Retention: If the product formed in a reaction has same stereochemistry as that of reactant, this process is called retention of configuration.

CHAME + (HI) + SKI HICH and

TOPIC-7

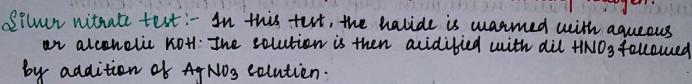
POLYHALOGEN COMPOUNDS:-

- (i) Dichlouomethane (CH2C12) is used as propellant in aerosous, as paint remover. Exposure to higher levels causes namea, dixiness.
- (ir) The tribategen derivatives of methane are called haloforms.

 eg:- CHUz (chleroform), CHIz (Iodoform, used as an antiseptic)
- (iii) Chloroform is stored in dark coloured bettles as in presence of light, it gets converted into highly poisonous substance, phosgene (coll)

 Preparation of phosgene:

- (iv) DDT is 1,1,1-trichloro-2,2-bis ethane (4-chlorophenyl) and is used as a powerful insertable.
- (V) CCly is used as a fire extinguisher under the name pyrene.
- (vi) Freen-12 (CF2U2) is used as a refrigerant.



· Alkyr, benzyl and allyl halides gine precipitate.
· Aryl and ninys halides denot gine precipitate.

* The precipitate formed should be insoluble in HNOg.

- (a):- How will you distinguish between the following pairs of compounds:
 - (1) Chloreform and carbon tetrachloride AM: - Invention o It the fuedu
 - (is Benzychleride and chlerobenzene
- Ans: (i) On heating theoroform with aniline and ethanoice KOH, it forms a pungent smelling isolyanide whoreas carson tetrachloride deernot gine this test.

CoH5NH2 + CHU3 + 3KOH (ethanolic) - CoH5NC + 3KCL + 3H2O Phenyl isocyanide (Pungent emeu) and the commence of the contract of the contra

(ii) On adding sedium hydroxide and eilner nitrate to both the compounds, bonzyl chloride forms white precipitate but chlorobenzene doesnot form unite precipitate.

CCH5CH2U+ NaOH -> C6H5CH2OH+ Nach Nau + AgNO3 - Agu + NaNOs

[In exam, you can either write the statement or the reaction]

By is not a spice the fisher where we are your proper.