ORGANIC CHEMISTRY

SOME NOTEWORTHY POINTS

2. If there are two or more functional groups, the order of decreasing priority is : –COOH > $-SO_3H$ > anhydride > Ester > Acid halide > nitrile > aldehyde > ketone > alcohol > amine >> $C = C < > - C \equiv C -$

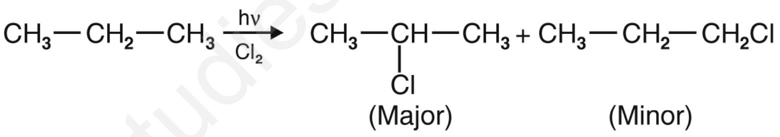
3. Anti Markownikov's addition takes place only with HBr in presence of a peroxide.

4. Order of reactivity of hydrohalic acid : HI > HBr > HCl.

5. Order of reactivity of alcohols with Lucas reagent : 3° > 2° > 1°.

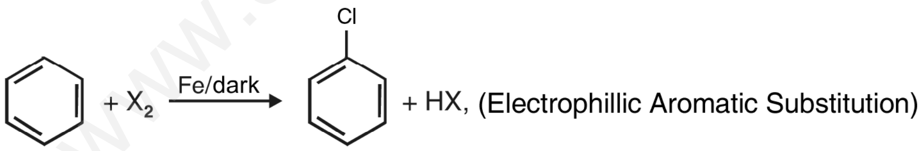
6. $R - H + X_2 \xrightarrow{h\nu} R - X + HX$. The order of reactivity of halogens $Cl_2 > Br_2 > I_2$. Order of reactivity of hydrogen atom substracted is 3° > 2° > I°.

Example :



$$CH_3-CH_2-CH_3 \xrightarrow[Cl_2]{h\nu} \underset{(\text{Major})}{CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3} + \underset{(\text{Minor})}{CH_3-CH_2-CH_2Cl}$$

7.



8. Order of reactivity in S_N1 and S_N2 mechanism are as follows :

$$\overset{\text{For } S_N1 \text{ reactions}}{\xleftarrow{\hspace{3cm}}}$$

$$3^\circ \qquad 2^\circ \qquad 1^\circ \qquad CH_3X$$

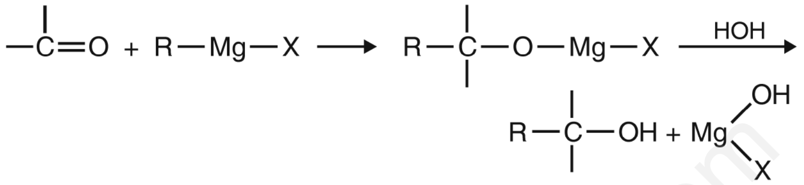
$$\underset{\text{For } S_N2 \text{ reactions}}{\xrightarrow{\hspace{3cm}}}$$

$R - I > R - Br > R - Cl.$

9. In case of optically active alkyl halide, S_N2 mechanism results in the inversion of configuration while S_N1 mechanism in racemisation.

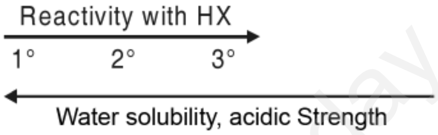
10. Aryl halides are much less reactive towards nucleopillic substitution reactions. Presence of electron withdrawing groups (like $-NO_2$, $-CN$, $-COOH$ etc.) at o– and/or *p*-position to halogen increases the rate of reaction.

12. All the three types of monohydric alcohols (1°, 2° or 3°) except methanol can be prepared from Grignard Reagent



$$>C=O + R-Mg-X \longrightarrow R-\overset{|}{\underset{|}{C}}-O-Mg-X \xrightarrow{HOH} R-\overset{|}{\underset{|}{C}}-OH + Mg\begin{matrix}OH\\X\end{matrix}$$

13. Alcohols



14. Presence of electron withdrawing group increases the acid strength of alcohol, phenol and carboxylic acid while presence of electron donating group decreases the acid strength.

E.W.G. : NO_2, $-X$, $-CN$, $-COOH$, etc., E.D.G. : $-R$, $-OR$, $-OH$, $-NH_2$ etc.

15. In electrophilic aromatic substitution reaction, ring activating groups like $-OH$, $-NH_2$, $-OR$, are o– and *p*– directing whereas ring deactivating groups like $-CHO$, $> C = 0$, $-COOH$, $-NO_2$, $-SO_3H$ are m-directing. Halogens (F, Cl, Br and I) are deactivating but are o– and p– directing groups.

16. 3° alcohols are resistant to oxidation due to lack of α-hydrogen.

17. Order of Acid strength : Alcohol < Phenol < Carboxylic acid, it is because of resonance stabilization of phenoxide and carboxylate ion. In carboxylate ion negative charge is delocalised over two oxygen atoms. while in phenoxide ion it is delocalised over one oxygen atom and the less electronegative C atom of benzene ring.

18. All organic compounds which form intermolecular H-bonds with water are soluble in water.

19. Intermolecular H-bonds of p- and m- nitrophenol increases water solubility/ Acid strength while intramolecular H-bonds in o-nitrophenol decreases

these properties.

20. In the reaction of alkyl aryl ether (Anisole) with HI, the products are always alkyl halide and phenol, because O–R bond is weaker than O–Ar bond.

22. In reaction of toluene with CrO_3 in presence of acetic anhydride is used to protect benzaldehyde as benzylidenediacetate to avoid further oxidation to benzoic acid.

23. Order of reactivity of aldehydes and ketones towards nuclerphilic attack

$HCHO > CH_3CHO > CH_3CH_2CHO$

RCHO > R COR ; ArCHO > Ar COR > Ar CO Ar.

because of (i) +I Inductive effect of alkyl groups. (ii) steric hindrance of alkyl and aryl group reactivity of ketones is less than aldelydes.

24. Bioling and melting points of various organic compounds depend on intermolecular forces of attraction which depend on the following :

(a) Inter molecular/intramolecular H-bonding.

(b) dipole-dipole interaction

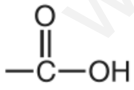
(c) Molecular size

(d) Surface area. (branching decreases surface area of molecules).

25. Benzaldehyde does not reduce Fehling's reagent.

26. The more the Ka value, the lesser is the pk_a, a stronger acid always has higher Ka but a lower pk_a value.

27. Order of Acid strength : $HCOOH > C_6H_5COOH > C_6H_5CH_2COOH > CH_3COOH, CH_3CH_2COOH$

28.  $-\overset{\overset{O}{\|}}{C}-OH$ group in carboxylic acid is not a true carbonyl group because of resonance.

Hence, carboxylic acids do not give addition reaction of aldehydes and ketones.

(a) In aqueous solution order of basicity is :

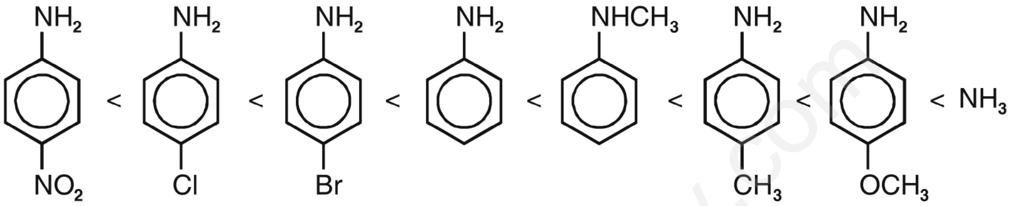
$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$.

(b) In gaseous (vapour) state order of basicity is :

$RNH_2 < R_2NH < R_3N$.

30. Basic character of aromatic amine



31. Hinsberg's reagent ($C_6H_5SO_2Cl$) is used to separate the mixtures of 1°, 2° and 3° amines.

32. Sulphanilic acid exists as zwitter ion, therefore it is amphoteric in nature.

33. Aryl diazonium salts are more stable than alkyl diazonium salts.

34. Aniline, phenol and benzoic acid do not show Friedel-Crafts Reaction.

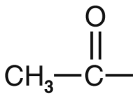
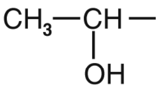
35. The more the basic character, the more is the K_b value and lesser will be its pk_b value.

35. In phenol and aniline, electron donating or electron withdrawing groups when present in ortho position, always have acid strenghening effect. This is called ortho effect.

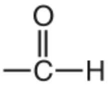
USEFUL TIPS FOR IDENTIFICATION OF FUNCTIONAL GROUPS

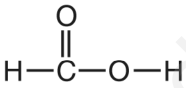
- For identification of chloro, bromo or Iodo alkanes, aq. KOH is added followed by $AgNO_3$ solution then precipitate of AgX is formed.

  Iodoform Test is given by all organic compounds having

   $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-$ or  $CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-$ when heated with NaOH (aq) and I_2, produces

  yellow iodoform (CHI_3)

- **Tollens' reagent** test is given by organic compound having  $-\overset{\overset{\displaystyle O}{\|}}{C}-H$ group

  (formic acid  $H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$ also gives this test).

  Tollens' reagent test is given by aldehydes

- Methanoic acid and ethanoic acid gives deep red colour solution with iron (III) chloride solution.
- Benzoic acid gives buff coloured precipitate with iron (III) chloride solution
- Acid chlorides and esters may be recognised after hydrolysis. The resultant acid and alcohol may be tested for.
- Amides are recognised by the liberation of ammonia on heating with alkali (NaOH or KOH) whereas ammonum salts liberate ammonia with alkali in the cold.
- 1°, 2° and 3° alcohols are distinguished by Lucas test.
- 1°, 2° and 3° amines can be distinguished with the help of Hinsberg reagent.
- 1° and 2° anines can be distinguished by Carbylamine test