

# Padasalai<sup>9</sup>S Telegram Groups!

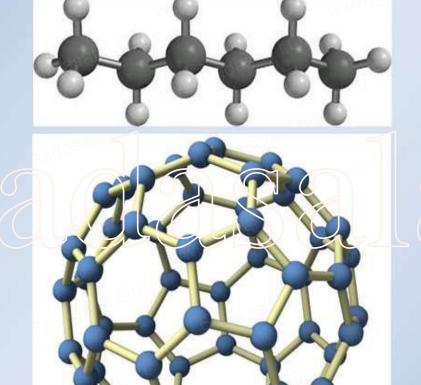
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- Padasalai's NEWS Group https://t.me/joinchat/NIfCqVRBNj9hhV4wu6\_NqA
- Padasalai's Channel Group <a href="https://t.me/padasalaichannel">https://t.me/padasalaichannel</a>
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# **ORGANIC CHEMISTRY**

STD - XI

UNIT - 12 & 13



## SHANMUGAM S

ST.JOHN'S MHSS PORUR CHENNAI -116 9841945665



## **Unit - 12**

## **Basic concepts of organic reactions**

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(A) 
$$CH_3CH_2CH_2Br + KOH \longrightarrow CH_2 = CH_2 + KBr + H_2O$$

(B) 
$$(CH_3)_3CBr + KOH \longrightarrow (CH_3)_3COH + KBr$$

(C) 
$$\longrightarrow$$
 + Br<sub>2</sub>  $\longrightarrow$   $\longrightarrow$  Br

Which of the following statement is correct?

- (a) (A) is elimination, (B) and (C) are substitution
- (b) (A) is substitution, (B) and (C) are elimination
- (c) (A) and (B) are elimination and (C) is addition reaction
- (d) (A) is elimination, B is substitution and (C) is addition reaction.
- 2. What is the hybridisation state of benzyl carbonium ion?
  - (a)  $sp^2$
- (b) spd<sup>2</sup>
- (c)  $sp^3$

(d) sp<sup>2</sup>d

- 3. Decreasing order of nucleophilicity is
  - (a)  $OH^- > NH_2^- > ^-OCH_3 > RNH_2$
- (b)  $NH_2^- > OH^- > ^-OCH_3 > RNH_2$
- (c)  $NH_2$  >  $CH_3O^-$  > OH- >  $RNH_2$
- (d)  $CH_3O^- > NH_2^- > OH^- > RNH_2$
- 4. Which of the following species is not electrophilic in nature?
  - (a) Cl<sup>+</sup>

- (b) BH<sub>3</sub>
- (c) H<sub>2</sub>O+

- (cl) + NO<sub>2</sub>
- 5. Homolytic fission of covalent bond leads to the formation of
  - (a) € lectrophile
- (b) nucleophile
- (c) Carbo cation
- (d) free radical

- 6. Hyper Conjugation is also known as
  - (a) no bond resonance

(b) Baker - nathan effect

(c) both (a)and (b)

- (d) none of these
- 7. Which of the group has highest +I effect?
  - (a) CH<sub>2</sub>-
- (b) CH<sub>3</sub>-CH<sub>2</sub>-
- (c)  $(CH_3)_2$ -CH-
- (d) (CH<sub>3</sub>)<sub>3</sub>-C-
- 8. Which of the following species does not exert a resonance effect?

(

- (a) C<sub>6</sub>H<sub>5</sub>OH
- (b)  $C_6H_5CI$
- $(c) C_6 H_5 N H_2$
- (d) C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub>

- 9. -I effect is shown by
  - (a) -Cl

- (b) -Br
- (c) both (a) and (b)
- (d) -CH<sub>2</sub>

- 10. Which of the following carbocation will be most stable?
  - (a) Ph<sub>a</sub>C -
- (b) CH<sub>2</sub>-CH<sub>2</sub>-
- (c) (CH<sub>3</sub>)<sub>2</sub>-CH
- (d) CH<sub>2</sub>= CH CH<sub>2</sub>
- 11. Assertion: Tertiary Carbocations are generally formed more easily than primary Carbocations ions. Reason: Hyper conjugation as well as inductive effect due to additional alkyl group stabilize tertiary carbonium ions.
- (a) both assertion and reason are true and reason is the correct explanation of assertion.
  - (b) both assertion and reason are true but reason is not the correct explanation of assertion.
  - (c) Assertion is true but reason is false
- (d) Both assertion and reason are false

12. Heterolytic fission of C-Br bond results in the formation of

(a) free radical

(b) Carbanion

(c) Carbocation

(d) Carbanion and Carbocation

13. Which of the following represent a set of nuclephiles?

(a) BF<sub>3</sub>, H<sub>2</sub>O, NH<sub>2</sub>

(b) AICI<sub>3</sub>, BF<sub>3</sub>, NH<sub>3</sub>

(c) CN -,RCH<sub>2</sub>-, ROH

(d) H+, RNH<sub>3</sub>+, :CCl<sub>2</sub>

14. Which of the following species does not acts as a nucleophile?

- (a) ROH
- (b) ROR
- (c) PCl<sub>2</sub>

(d) BF,

15. The geometrical shape of carbocation is

- (a) Linear
- (b) tetrahedral
- (c) Planar
- (d) Pyramidal

16. Write short notes on (a) Resonance (b) Hyperconjucation

(a) Resonance

Certain organic compounds can be represented by more than one structure and they differ only in the position of bonding and lone pair of electrons. Such structures are called resonance structures

(b)Hyperconjucation The delocalisation of electrons of **♂** bond is called as hyper conjugation

17. What are electrophiles and nucleophiles? Give suitable examples for each.

Electrophiles:

Electrophiles are reagents that are attracted towards negative charge or electron rich center.

They are either positively charged ions or electron deficient neutral molecules

**Neutral electrophiles** 

: AICI<sub>3</sub>, CO<sub>2</sub>, BF<sub>3</sub>, FeCI<sub>3</sub>, : CCI<sub>4</sub>

Positively charged electrophiles

: R<sup>+</sup>, H<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, NO<sub>2</sub><sup>+</sup>

**Nucleophiles:** 

Nucleophiles are reagents that has high affinity for electro positive centers.

**Neutral Nucleophiles** 

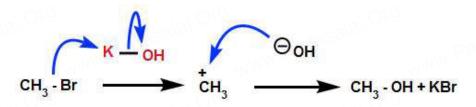
: H<sub>2</sub>O, R-OH, NH<sub>2</sub>, R-O-R,

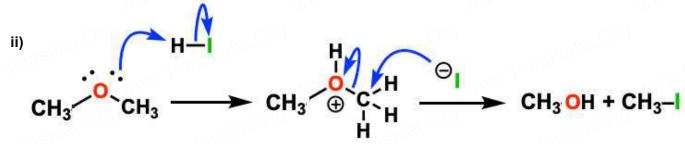
Negatively charged nucleophiles

: OH<sup>-</sup>, Cl<sup>-</sup>, CN<sup>-</sup>, RCOO<sup>-</sup>, RO<sup>-</sup>

18. Show the heterolysis of covalent bond by using curved arrow notation and complete the following equations. Identify the nucleophile is each case.

i)





## 19. Explain inductive effect with suitable example.

Inductive effect is defined as the change in the polarisation of a covalent bond due to the presence of adjacent bonds, atoms or groups in the molecule. This is a permanent phenomenon.

Their ability to release or withdraw the electron through sigma covalent bond is called +I effect and

## - I effect respectively

Electron withdrawing or - I group: -F, -CI, -COOH, -NO<sub>2</sub>, NH<sub>2</sub>

Electron donating or + I groups : CH<sub>3</sub>O<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>O<sup>-</sup>, COO<sup>-</sup> etc

The order of the -I effect of some groups are given below

$$NH_3^+ > NO_2 > CN > SO_3H > CHO > CO > COOH > COCI > CONH_2 > F > CI > Br > I > OH > OR > NH_2 > C_EH_5 > H$$

The relative order of +I effect of some alkyl groups is given below

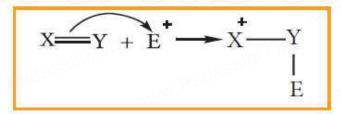
$$-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$$

## 20. Explain electromeric effect.

Electromeric effect is a **temporary effect** and observed only in organic compounds with multiple bonds in the presence of an attacking reagent.

## + ve Electromeric effect.

When the **G** electron is transferred towards the attacking reagent, it is called - E (positive electromeric) effect.



## - ve Electromeric effect.

When the  $\pi$  electron is transferred away from the attacking reagent, it is called, -E (negative electromeric) effect

$$Nu + X = Y \rightarrow X - Y$$

## 21. Give examples for the following types of organic reactions

(i)  $\beta$  - elimination (ii) electrophilic substitution.

(i) 
$$CH_3$$
  $CH_2$   $CH_2$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_4$   $CH_5$   $CH_5$   $CH_5$   $CH_6$   $CH_7$   $CH_8$   $CH_$ 

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# **Hydrocarbons**

#### Give IUPAC names for the following compounds 31.

- 1) CH<sub>3</sub>-CH=CH-CH=CH-C = C-CH<sub>3</sub>
  - Octa 2,4 diene 6-yne
- 2)  $CH_3 C C C = C CH_3$   $CH_3 + H$
- 2-ethyl -2,4 -dimethyl hex-4-yne
- 3)  $(CH_3)_3 C H C = C CH (CH_3)_2$  2,5-dimetyl-hex-3-yne
- 4) ethyl isopropyl acetylene
- 2,2-dimethyl-hex-3-yne
- 5)  $CH \equiv C C \equiv C C \equiv CH$
- 1,3,5 hexatriyne

#### 32. Identify the compound A, B, C and D in the following series of reactions

$$CH_{3}-CH_{2}-Br \xrightarrow{alc\ KOH} CH_{2}=CH_{2} \xrightarrow{Cl_{2}/CCl_{4}} CI-CH_{2}-CH_{2}-CH_{2}-CH=CH$$

$$CH_{2}=CH_{2}+O_{3} \xrightarrow{CH_{2}} CH_{2} \xrightarrow{Zn/H_{2}O} 2 \text{ HCHO}$$

### A- Ethene

- D ethyne

#### 33. Write short notes on ortho, para directors in aromatic electrophilic substitution reactions.

Those which increases electron density at 'ortho' and 'para' position are known as ortho-para directors All the activating groups are 'ortho-para' directors.

Let us consider the directive influences of phenolic (-OH) group. Phenol is the resonance hybrid of following structures.

#### 34. How is propyne prepared from an alkylene dihalide?

35. An alkylhalide with molecular formula  $C_6H_{13}Br$  on dehydro halogenation gave two isomeric alkenes X and Y with molecular formula  $C_6H_{12}$ . On reductive ozonolysis, X and Y gave four compounds  $CH_3COCH_3$ ,  $CH_3CHO$ ,  $CH_3CHO$ ,  $CH_3CHO$  and  $(CH_3)_2CHCHO$ . Find the alkylhalide.

$$CH_3 - CH - CH - CH_2 - CH_3 \xrightarrow{\text{halogenation}} CH_3 - C = CH - CH_2 - CH_3 + CH_3 - CH - CH = CH - CH_3$$

$$CH_3 - CH - CH - CH_2 - CH_3 + CH_3 - CH - CH = CH - CH_3$$

$$CH_3 - CH - CH_2 - CH_3 + CH_3 - CH - CH = CH - CH_3$$

$$CH_3 - CH - CH_2 - CH_3 + CH_3 - CH - CH_3 - CH - CH_3 - CH - CH_3$$

$$CH_3 - CH - CH_3 - CH - CH_3$$

$$CH_3 - CH - CH_3 - CH - CH_3$$

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$$CH_3 - CH - CH_3 - CH - CH_3$$

$$CH_3 - CH - CH_3 - CH - CH_3$$

$$CH_3 - CH - CH_3 - CH - CH_3$$

$$CH_3 - CH - CH_3$$

$$CH$$

36. Describe the mechanism of Nitration of benzene.

## Step 1:

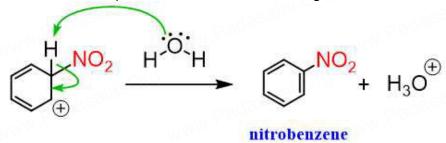
Nitric acid accepts a proton from sulphuric acid and then dissociates to form nitronium ion.

$$HO-S-O-H$$
 +  $H-O-N-O-H$  +  $H-O-N-O-H$  +  $H_2O-N-O-H$  +  $H_2O-N-O-H$  Nitronium ion

## Step 2:

The nitronium ion acts as an electrophile in the process which further reacts with benzene to form an arenium ion.

The arenium ion then loses its proton to Lewis base forming nitrobenzene.



- 37. How does Huckel rule help to decide the aromatic character of a compound.
  - i) Presence of (4n+2)  $\pi$  electrons in the ring where n is an integer (n=0,1,2...)
  - ii) All carbon atoms should be sp<sup>2</sup> hyberdised.
  - iii) System should be cyclic.
  - iv) System should have conjugation.

**Example:** (i) The benzene is a planar molecule

- (ii) It has six deloclaised  $\pi$  electorns
- (iii) 4n + 2 = 6 4n = 6 2 4n = 4

n = 1 it obeys Huckel's (4n+2) p electron rule with n = 1 hence, benzene is aromatic.



## 38. Suggest the route for the preparation of the following from benzene.

1) 3 - chloro nitrobenzene

2) 4 - chlorotoluene

3) Bromo benzene

4) m - dinitro benzene

## 1) Benzene conver into 3- chloronitro benzene

2) Benzene conver into 4 - chlorotoluene

3) Benzene conver into Bromo benzene

4) Benzene conver into m - dinitro benzene

$$\frac{\text{conc.HNO}_3/\text{H}_2\text{SO}_4}{\text{H}_2\text{SO}_4\text{ \& heat}} \xrightarrow{\text{NO}_2} \frac{\text{NO}_2}{\text{NO}_2}$$

## 39. Suggest a simple chemical test to distinguish propane and propene.

Propene (unsaturated) is an alkene, whereas propane (saturated) is an alkane

Add bromine water (brown) to the test tubes

If the bromine water stays brown, the test tube contains propane

If the bromine water goes colourless, the test tube contained propene

## 40. What happens when isobutylene is treated with acidified potassium permanganate?

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 - \text{C= CH}_2 \end{array} \xrightarrow{\text{KMnO}_4/\text{H}^+} \text{CH}_3 \text{CO CH}_3 + \text{H-COOH} \xrightarrow{\text{O}_2} \text{CO}_2 + \text{H}_2\text{O} \end{array}$$

## 41. How will you convert ethyl chloride in to i) ethane ii) n- butane

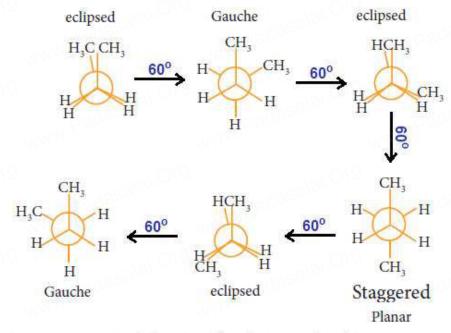
i) Ethyl chloride in to ethane

$$CH_3$$
- $CH_2$ - $CI$   $\xrightarrow{alc KOH}$   $CH_2$  =  $CH_2$   $\xrightarrow{H_2/Ni}$   $CH_3$ -  $CH_3$ 

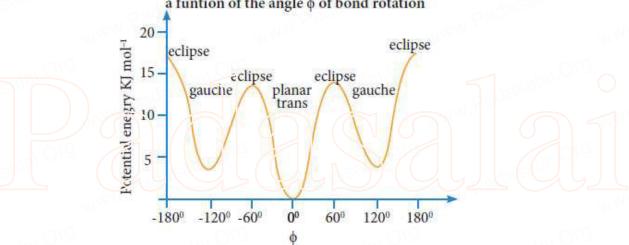
ii) Ethyl chloride into n-butane

Wurtz reaction.

## 42. Describe the conformers of n - butane.



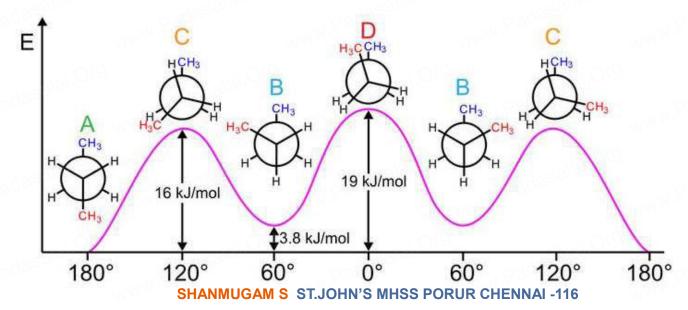
potential energy of a n-butane molecules as a funtion of the angle  $\phi$  of bond rotation



## **Conformations of n-Butane:**

potential energy difference : Eclipsed > Gauche > Staggered

Stability order : Staggered > Gauche > Eclipsed



## 43. Write the chemical equations for combustion of propane

propane 
$$CH_3$$
- $CH_2$ - $CH_3$  + 5  $O_2$   $\longrightarrow$  3  $CO_2$  + 4  $H_2O$ 

## 44. Explain Markownikoff's rule with suitable example.

"When an unsymmetrical alkene reacts with hydrogen halide, the hydrogen adds to the carbon that has more number of hydrogen and halogen add to the car- bon having fewer hydrogen".

This rule can also be stated as in the addition reaction of alkene / alkyne, the most electro negative part of the reagent adds on to the least hydrogen attached doubly bonded carbon.

The order of reactivity of diff erent hydrogen halides is HI > HBr > HCl.

## Example:

CH<sub>3</sub>-CH = CH<sub>2</sub> + HBr 
$$\longrightarrow$$
 CH<sub>3</sub>- CH - CH<sub>3</sub> + CH<sub>3</sub>-CH<sub>2</sub>- CH<sub>2</sub> Br

Br

2-Bromo Propane
(major product)

1-Bromo Propane
(Minor Product)

## Mechanism:

Step: 1 Formation of electrophile:  $HBr \longrightarrow H^+ + Br^-$ 

**Step:2** Secondary carbocation is more stable than primary carbocation and it predominates over a the primary carbocation.

CH<sub>3</sub>-CH = CH<sub>2</sub> + H<sup>+</sup> 
$$\longrightarrow$$
 CH<sub>3</sub>-CH<sub>2</sub>-  $\overset{+}{\text{CH}}_2$  1° carbocation

CH<sub>3</sub>-  $\overset{+}{\text{CH}}$  - CH<sub>3</sub> 2° carbocation

Step:3 The Br = ion attack the 2° carbocation to from 2 -Bromobutane, the major product.

CH<sub>3</sub>-  $\overset{+}{\text{CH}}$  - CH<sub>3</sub> + Br =  $\overset{+}{\text{CH}}$  - CH<sub>3</sub>

45. What happens when ethylene is passed through cold dilute alkaline potassium permanganate.

$$H_2C = CH_2 + (O) + H_2O$$
 alkaline KMnO<sub>4</sub>  $CH_2 - CH_2$  OH OH

46. Write the structures of following alkanes.

2) 5 - (2 - Ethyl butyl) - 3, 3 - dimethyldecane

$$\begin{array}{c} \mathsf{CH_2\text{-}\,CH_3} \\ \mathsf{CH_3} & \mathsf{CH_2\text{-}CH - CH_2\text{-}CH_3} \\ \mathsf{CH_3\text{-}\,CH_2 - C - CH_2\text{-}CH - CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3} \\ \mathsf{CH_3} \end{array}$$

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3) 5 - (1, 2 - Dimethyl propyl) - 2 - methylnonane

$$\begin{array}{c} \mathsf{CH_3} \ \mathsf{CH_3} \\ \mathsf{CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH\text{-}CH\text{-}CH\text{-}CH_3} \\ \mathsf{CH_2} \\ \mathsf{CH_2\text{-}CH\text{-}CH_3} \\ \mathsf{CH_3} \\ \mathsf{CH_3} \end{array}$$

47. How will you prepare propane from a sodium salt of fatty acid?

Sodium butanoate ( sodium salt of butanoic acid ) on heating with sodalime yields propane by decarboxylation.

$$\mathsf{CH_3CH_2CH_2COONa} \ \underline{\hspace{1.5cm} \mathsf{CaO}\,/\mathsf{NaOH}} \ \mathsf{CH_3CH_2CH_3} + \mathsf{Na_2CO_3}$$

48.  $CH_3 - CH (CH_3) - CH (OH) - CH_3 \xrightarrow{H^+/heat}$  (A) major product  $\xrightarrow{HBr}$  (B) major product

A Charles Objections

A- 2-methyl-2-butene B- 2-Bromo -2- methyl-2-butane

- 49. Complete the following:
  - i) 2 butyne Lindlar Catalyst
  - ii)  $CH_2 = CH_2 \xrightarrow{l_2}$
  - iii)  $CH_2 Br = CH_2 Br \underline{Zn/C_2 H_5 OH}$
  - iv) CaC<sub>2</sub> H<sub>2</sub>O

CH<sub>3</sub>-C
$$\equiv$$
C-CH<sub>3</sub> +H<sub>2</sub> Pd-CaCO<sub>3</sub> H Cis-2-butene CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub>

ii) 
$$CH_2 = CH_2 \xrightarrow{I_2} \begin{bmatrix} CH_2 - CH_2 \\ I & I \end{bmatrix} \xrightarrow{CH_2 = CH_2} CH_2 = CH_2$$
 ethene

- 50. How will you distinguish 1 butyne and 2 butyne?
  - i) 1-butyne and 2-Butyne are distinguished by "Tollins reagent test ".
  - 1-butyne gives tollins reagent test but 2-Butyne doesn't.
  - ii) There will be no reaction between butene-2 and  $\mathrm{Cu_2Cl_2}$  because it has no acidic hydrogen. In butyne-1 the terminal hydrogen is acidic ( $\mathrm{CH_3CH_2}$ -C= CH) so it will give a real ppt with ammonical  $\mathrm{Cu_2Cl_2}$

CH<sub>3</sub>-CH<sub>2</sub>-C
$$\equiv$$
CH + 2AgNO<sub>3</sub> + 2NH<sub>4</sub>OH  $\longrightarrow$  CH<sub>3</sub>-CH<sub>2</sub>-C $\equiv$ C-Ag  $\downarrow$  Silver butynide  $+$  2 NH<sub>4</sub>NO<sub>3</sub> + 2H<sub>2</sub>O CH<sub>3</sub>-CH<sub>2</sub>-C $\equiv$ CH + Cu<sub>2</sub>Cl<sub>2</sub> + 2NH<sub>4</sub>OH  $\longrightarrow$  CH<sub>3</sub>-CH<sub>2</sub>-C $\equiv$ C-Cu  $\downarrow$  Copper butynide  $+$  2 NH<sub>4</sub>NO<sub>3</sub> + 2H<sub>2</sub>O CH<sub>3</sub>-C $\equiv$ C-CH<sub>3</sub> + 2AgNO<sub>3</sub> + 2NH<sub>4</sub>OH  $\longrightarrow$  No Raection due to absence of acidic hydrogen 2-butyne

