

### **HINTS & SOLUTIONS**

# EXERCISE - 1 Single Choice

26. Nucleophilicity ∝ Size (in group)

- 31. According to carboction stability IV > III > II > I
- **32.** According to carbocation stability

33. 
$$Ph \xrightarrow{CH_3} Ph \xrightarrow{CH_3} Ph \xrightarrow{CH_3} Ph \xrightarrow{Et} Br$$
(Chiral carbon atom) 
$$Ph \xrightarrow{CH_3} Ph \xrightarrow{CH_3} Ph$$

35.  $CH_3 - CH_2 - CH_2 - CH_2 - OH \xrightarrow{NaBr, H_sSO_4} CH_3 - CH_2 - CH_2 - Br$  unbranched 1° alcohol give  $S_N2$  reaction with HX.

36. 
$$SOCl_2$$
 Pyramid,  $\Delta$   $CH_2 - Cl$ 

It is  $S_N 2$  reaction.

37.  $H \xrightarrow{CH_3} OH \xrightarrow{PCl_5} Cl \xrightarrow{H_5} H$  Product is R - 2- Chlorobutane  $C_2H_5 \qquad C_3H_5$ 

It is S<sub>N</sub>2 reaction

39. 
$$H_{5}C_{6} \xrightarrow{\text{OH}} \xrightarrow{\text{SOCl}_{2}} H_{5}C_{6} \xrightarrow{\text{CH}_{3}} CI$$

It is  $S_N$ i mech so retention of configuration

40. 
$$CH_3 - CH_2 - CH - CH_3 \xrightarrow{SOCl_2} CH_3 - CH_2 - CH - CH_3$$
It is S<sub>N</sub>i mech so retention of configuration.

41. 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3 \xrightarrow{HCI/\Delta} CH_3 - CH_2 - CH_2 - OH + CH_3 - CH_2 - CI$$

42. 
$$CH_3$$
  $CH_2$   $CH_2$   $CH_3$   $CH_3$   $CH_3$   $CH_4$   $CH_5$   $CH_5$   $CH_5$   $CH_5$   $CH_6$   $CH_6$   $CH_7$   $CH_8$   $CH_$ 

In acidic medium  $S_N 1$  type product,  $N_u^{\Theta}$  attack from crowded side.

- **43.** According to stability of carbocation.
- 44. Ring expansion so q will migrate.

45. 
$$\begin{array}{c} CH_2OH \\ \hline \\ -H_2O \end{array}$$
 
$$\begin{array}{c} CH_3 \\ \hline \\ -H_2O \end{array}$$

47. CH<sub>3</sub>-C-CH<sub>2</sub>-CH<sub>3</sub> alc. KOH/
$$\triangle$$
 CH<sub>3</sub>-CH=C-CH<sub>3</sub> + H<sub>2</sub>C=CH-CH<sub>2</sub>-CH<sub>3</sub>
Cl CH<sub>3</sub>

48. (a) 
$$\stackrel{\text{OH}}{\longrightarrow}$$
  $\stackrel{\text{H}^{\oplus}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{CH}_2 - \text{Br}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{CH}_2 - \text{Br}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{CH}_2 - \text{Br}}{\longrightarrow}$   $\stackrel{\text{OH}}{\longrightarrow}$   $\stackrel{\text{CH}_3 - \text{Br}}{\longrightarrow}$   $\stackrel{\text{CH}_3 - \text$ 

49. In case of  $S_N$ i no inverson occurs but in presence of pyridine  $S_N$ 2 reaction takes place and configuration is inverted.

50. Me 
$$\xrightarrow{H^{\circ}}$$
 Me  $\xrightarrow{Me}$  Me

Total 9 alkenes are formed and after fractional distillation 6 are separated.

53. 
$$Me - CH = CH - CH_2 - CI \xrightarrow{EtOH} Me - CH = CH - CH_2 \longleftrightarrow Me - CH - CH = CH_2 \\ \downarrow EtOH & \downarrow Et - OH \\ Me - CH = CH - CH_2 & Me - \ref{ch} - CH = CH_2 \\ \downarrow OEt & OEt \\ (cis + trans) & (d + \ell) mix.$$

54. 
$$CH_3 - CH_2 - \ddot{O} + ZnCl_2 \longrightarrow CH_3 - CH_2 - \ddot{O} - ZnCl_2 \xrightarrow{Cl^{\Theta}} CH_3 - CH_2 - Cl + HOZnCl_2$$

55. Strength of Nucleophile generally increases on going down a group in the periodic table, so (D) is not true.

56. 
$$\text{Cl-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{\text{NaOH}} \text{Cl-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-ONa} \xrightarrow{\text{O'}}$$

strong anionic nucleophile and 1° alkyl halide favours S<sub>N</sub>2 mechanism.

- 58. Nucleophilic substitution of alcohol is acid catalysed reaction.
- **59.** Bridge head carbocation is not formed.

60. 
$$CH_2OH$$

$$SOCI_2$$

$$pyridine$$

$$(S_N2)$$

$$OCH_3$$
 $CH_2CI$ 

$$+ SO_2 + HO$$

61. I  $\Rightarrow$  Only one T.S. So it is for  $S_N^2$  and  $\Delta H = -ve$ . II  $\Rightarrow$  Only one T.S. So it is for  $S_N^2$  and  $\Delta H = +ve$ . III  $\Rightarrow$  More than one T.S. so it is for  $S_N^1$  and 1st step is rds.

**63.** Correct Product for (C) option.

64. 
$$Ph\text{-O-CH}_2\text{-CH}_2\text{-OH} \xrightarrow{H^{\oplus}} Ph\text{-O-CH}_2\xrightarrow{\oplus} Ph\text{-O-CH-CH}_3 \xrightarrow{B^{\oplus}_{\Gamma}} Ph\text{-O-CH-CH}_$$

## EXERCISE - 2 Part # I : Multiple Choice

- 1. Nucleophiles are electron rich species.
- 2. Anionic nucleophiles are better than their neutral nucleophiles.

$$\begin{array}{c} Me \\ Me \\ OH \\ H \\ OCH_3 \end{array}$$

4. 
$$CH_3$$
 OH  $CH_3$  OTs  $CH_3$   $CH_3$ 

### **CHEMISTRY FOR JEE MAIN & ADVANCED**

5. 
$$CH_{3} \xrightarrow{CH_{3}} OH \xrightarrow{CH_{3}OH} CH_{3} \xrightarrow{CH_{3}OH} CH_{3} \xrightarrow{CH_{2}} CH_{2} \xrightarrow{H_{2}O^{18}} CH_{3} \xrightarrow{CH_{3}OH} CH_{3} \xrightarrow{CH_{$$

- 7. Rate of  $E^2$  reaction  $\infty$  Stability of alkene
- **8.** All statement are correct.
- 9. 1° alkyl halide is more reactive than 2° alkyl halide. So transition state in II reaction is more stable than I reaction.

10. 
$$CH_{3} - CH - CH_{2} \xrightarrow{CH_{3}-C^{\circ}C^{-}} CH_{3} - CH - CH_{2} - C \equiv C - CH_{3} \xrightarrow{CH_{3}I} CH_{3} - CH - CH_{2} - C \equiv C - CH_{3}$$

$$OCH_{3} = CH - CH_{2} - C \equiv C - CH_{3}$$

$$OCH_{3} = [Y]$$

11. Product mixture

$$MeO \longrightarrow H_3C H H$$

$$MeO \longrightarrow HOH D$$

Product mixture react with  $PCl_5$  by  $S_N^2$  mechanism and four products are formed. They are positional isomers and diastereomers so after fractional distillation four fraction are obtained.

12. Correct product for (B) option.

$$CH_3$$
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

Option (D) is also not feasible because aromatic halide do not given SN reaction in normal condition.

13. 
$$CH_3 CH_2O + CH_3 - CH_2 - CI \xrightarrow{S_N^2} CH_3 - CH_2 - O - CH_2 - CH_3$$

$$\begin{array}{c} CH_3 \\ CH_3 - C - CH_2 - CH_2 \ Br + NH_3 \xrightarrow{S_N 2} CH_3 - C - CH_2 - CH_2 - NH_2 \\ CH_3 \end{array}$$

$$CH_3 - CH_2 - OH + HBr \xrightarrow{S_N 2} CH_3 - CH_2 - Br + H_2O$$

14. 
$$\begin{array}{c} CH_{3} \\ H \\ CH_{3} \\ CH_{3} \end{array} \xrightarrow{CH_{3}} CH_{3} CH$$

#### Part # II: Assertion & Reason

- **6.** S-1 and S-2 is correct and S-2 is correct explanation of S-1.
- 7. S-1 is true and S-2 is false.

  The transition state for the anti-periplanar arrangement is a staggered conformation, with the base far away from the leaving group. In most cases, this transition state is lower in energy than that for the syn-periplanar elimination.
- 8.  $S_{N}^{2}$  is not possible at 3° alkyl halide by strong base.
- 9. Alcohol give S<sub>N</sub> reaction only in acidic medium.
- 10. Polar aprotic solvent is used for  $S_N^2$  reaction because they do not solvate the anion appreciable
- 11. By going top to bottom in periodic table nucleophilicity increases (in protic solvent) because polarisability increases and Iodide is weakly solvated in a protic solvent.

#### **EXERCISE - 3**

#### Part # I: Matrix Match Type

3. Weak neutral nucleophile  $\Rightarrow$  S<sub>N</sub>1, so rearrangement is possible.

Strong anionic nucleophile  $\Rightarrow$  S<sub>N</sub>2, walden inversion is possible.

Strong anionic nucleophile  $\Rightarrow$  S<sub>N</sub>2 but  $\alpha$  carbon is not stereogenic.

Aq. NaOH  $\Rightarrow$  S<sub>N</sub>1, carbocation is already stable so no rearrangement.

- 4. 1° Alkyl halide and anionic strong nucleophile  $\Rightarrow$  S<sub>N</sub>2
  - $2^{\circ}$  Alkyl halide and anionic strong base  $\Rightarrow E^2$
  - 3° Alcohol and acidic medium  $\Rightarrow$  E<sup>1</sup>
  - 3° Alkyl halide and weak neutral nucleophile  $\Rightarrow$  S<sub>N</sub>1

#### Part # II : Comprehension

#### Comprehension #1:

1. 
$$CH_{3} - CH - CH - CH_{3} \xrightarrow{H^{\oplus}} CH_{3} - CH - CH_{3} \xrightarrow{\oplus} CH_{3} - CH_{3} \xrightarrow{\oplus} CH_{3} - CH_{2} - CH_{3}$$

$$CD_{3} \qquad CD_{3} \qquad CD_{3} \qquad CD_{3}$$

2. Most stable alkene (saytzeff alkene) is major product.

$$\begin{array}{c} CH_3 \text{ OH} \\ H_3C - C - C - CH_3 \xrightarrow{H^{\oplus}} H_3C - C - CH - CH_3 \xrightarrow{\oplus} H_3C - CH_3 \xrightarrow{\oplus} CH_3 \xrightarrow{CH_3} H \xrightarrow{CH_3} CH_3 \end{array}$$

$$\longrightarrow H_3C - C = C - CH_3 \xrightarrow{CH_3} CH_3$$

$$(\text{major product})$$

3. In this reaction pinacol pinacolone rearrangement takes place

$$\bigcirc \text{OH} \xrightarrow{\text{H}_{\oplus}} \bigcirc \text{OH} \longrightarrow \bigcirc \stackrel{\text{H}}{\longrightarrow} \text{OH} \longrightarrow \bigcirc \stackrel{\text{H}}{\longrightarrow}$$

# EXERCISE - 4 Subjective Type

- 1.  $S_N^2$  attack on a carbon of benzene ring does not occur nor does the high energy  $C_6^4H_5^+$  form by an  $S_N^4$ 1 reaction. Hence ArI cannot be a product even in an excess of conc. HI.
- 2. (a)  $CH_3$  (b)  $CH_3$   $C-CH_2CH_3$   $CH_3$
- 3. (a) OH OH OH
- **4.** (A)  $C_2H_5Cl$ ; (B)  $C_2H_5CN$ ; (C)  $C_2H_5COOH$ ; (D)  $C_2H_5COONH_4$ ; (E)  $C_2H_5CONH_2$
- 5. (A) C<sub>3</sub>H<sub>7</sub>Br; (B) CH<sub>3</sub>CH=CH<sub>2</sub>; (C) CH<sub>3</sub>CHBrCH<sub>3</sub>; (D) CH<sub>3</sub>CHNH<sub>2</sub>CH<sub>3</sub>
- 6. The +I.E. of three methyl groups on central C-atom of tert-butyl alcohol makes is partially negative with the result that it pushes the electron pair of –OH bond towards H-atom and thus H-atom is not replaced easily.
- 8.  $CH_3 \longrightarrow CH_3 \longrightarrow CH_3$

(nucleophile attacks the more substituted carbon in acid-catalysed reaction)

(nucleophile attacks the less substituted carbon in base-catalysed reaction)

- **9.** I: bond b ; II: bond a
- 10. A is laevo isomer
- 11.  $H_2C=CH-CH-CH_3$   $\xrightarrow{H^+}$   $H_3C-CH-CH_3$   $\xrightarrow{\tilde{\cdot}_{:H}}$   $H_3C-CH_2$   $\overset{-}{C}-CH_3$   $H_3C-CH_3$   $H_3C-CH_3$   $H_3C-CH_3$   $H_3$

#### **CHEMISTRY FOR JEE MAIN & ADVANCED**

$$\xrightarrow{H_2O} H_3OH_2-C-CH_3$$

$$Ph$$

(Hydration gives an intermediate 2 C<sup>+</sup>, which undergoes a hydride shift Although phenyl is a better migrator than H, migration of H occurs leading to a more stable 3 benzylic carbocation.)

Bond energy of C (vinylic)—O bond ( $\alpha$ ) is greater than that of C(alkylic)—O bond ( $\beta$ ). Hence, when A reacts with HI, bond  $\beta$  breaks forming B.

13. CH<sub>2</sub>O<sup>-</sup> (nucleophile) attacks less submituted carbon (which is C-14 in this case) forming intermediate (C).

(C) will displace Cl<sup>-</sup> forming (B)

 $\begin{array}{ccc} \textbf{14.} & \textbf{C}_2\textbf{H}_5\textbf{OH} & \textbf{C}_2\textbf{H}_5\textbf{Cl} \\ & \textbf{Ethyl alcohol} & \textbf{Ethyl chloride} \end{array}$ 

 $(X) \qquad \qquad (Y)$ 

15.  $(CH_3)_2CHCH_2OH;$   $(CH_3)_2C=CH_2;$   $(CH_3)_3COH$  (A) (B) (C)

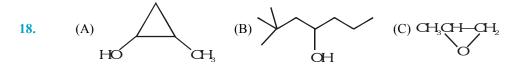
Synchronous migration of Ph provides greater assistance in the removal of H<sub>2</sub>O form the protonated alcohol

17. 
$$CH_2$$
  $CH_3CO_3H$   $CH_2$ = $CH_2$   $CH_3CH_2MgBr$ 

(B) (A)

 $A + B \xrightarrow{H_2O} CH_3CH_2CH_2CH_2OH$ 

(C)



19. 3 alcohol at  $C_2$  is more basic than 2 alcohol at  $C_5$ . Hence, intramolecular dehydration takes place such that H of 2 alcoholic group at  $C_5$  eliminates OH of 3 alcoholic groups at  $C_2$  (with isotopic <sup>18</sup>O) to form cyclic ether

**20.** A is a mixture of d- and 1- and thus racemic mixture.

# EXERCISE - 5 Part # I : AIEEE/JEE-MAIN

- 1.  $R OH \xrightarrow{H^{\oplus}} R OH_2$  this step is initiation step.
- 2. According to stability of carbocation.
- 3. Nucleophilicity order

$$CH_3O^{\Theta} > CN^{\Theta} > CH_3 - C - O^{\Theta} > CH_3 - O^{\Theta}$$

It is anti elimination reaction so hydrogen atom from second carbon will not eliminated as it is in syn-position rather hydrogen atom from 5<sup>th</sup> carbon will be eliminated.

### **CHEMISTRY FOR JEE MAIN & ADVANCED**

- Reaction of alcohol with HCl and anhydrous ZnCl<sub>2</sub> is an S<sub>N</sub> reaction.
   3° alcohol react faster with HCl and anhydrous ZnCl<sub>2</sub> since it forms more stable carbocation intermediate.
- 7.  $RS^{\Theta}$  is more nucleophilic than  $R-O^{\Theta}$  due to larger size of orbitals and polarization but  $RS^{\Theta}$  is less basic than  $R-O^{\Theta}$  as the negative charge get stabilized due to larger size of sulphur atom.
- 8. The reaction of alcohol with lucas reagent is mostly an  $S_N^1$  reaction and the rate of reaction is directly proportional to the carbocation stability formed in the reaction, since  $3^{\circ}$  R–OH forms  $3^{\circ}$  carbocation hence it will react fastest.

9. 
$$OH \longrightarrow CO_{2}H$$

$$CO_{2} \longrightarrow Salicyclic acid$$

$$(X)$$

This is called Kolbe reactions.

$$\begin{array}{c} OH \\ O-C-CH_3 \\ CO_2H \\ + (CH_3CO)_2O + concH_2SO_4 \longrightarrow \\ \hline (X) \\ \end{array}$$

$$\begin{array}{c} O-C-CH_3 \\ CO_2H \\ \hline \\ Aspirin \\ (non-narcotic analgesic) \\ \end{array}$$

This step is called acylation reaction.

10. 
$$\begin{array}{c} OH \\ + Cl - C - O - Me + NaOH \longrightarrow O - C - O - Me \\ \hline Methylchloroformate \end{array}$$

This step involves acid base reaction at first followed by S<sub>N</sub>AE reactions.

$$O \longrightarrow C \longrightarrow OMe$$

$$O \longrightarrow OM$$

This step is called bromination.

#### Part # II : IIT-JEE ADVANCED

5. 
$$\begin{array}{c} & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

$$[X] \xrightarrow[CH_3COOH]{O} \xrightarrow{NaOH} O$$

9. Ph 
$$\xrightarrow{OH}$$
  $\xrightarrow{CH_3}$   $\xrightarrow{H_2SO_4}$   $\xrightarrow{Ph}$   $\xrightarrow{OH}$   $\xrightarrow{CH_3}$   $\xrightarrow{Ph}$   $\xrightarrow{CH_3}$   $\xrightarrow{Ph}$   $\xrightarrow{CH_3}$   $\xrightarrow{Ph}$   $\xrightarrow{OH}$   $\xrightarrow{OH}$   $\xrightarrow{Ph}$   $\xrightarrow{OH}$   $\xrightarrow{OH}$   $\xrightarrow{OH}$   $\xrightarrow{Ph}$   $\xrightarrow{OH}$   $\xrightarrow$ 

### **MOCK TEST**

- 7.  $CH_3 CH_2 CH_2 CH_2 OH \xrightarrow{NaBr, H_3SO_4} CH_3 CH_2 CH_2 Br$  unbranched 1° alcohol give  $S_N$ 2 reaction with HX.
- 8.  $CH_3 CH_2 CH CH_3 \xrightarrow{SOCl_2} CH_3 CH_2 CH CH_3$ It is S<sub>N</sub>i mech so retention of configuration.

9. 
$$\begin{array}{c} CH_2OH \\ \hline \\ -H_2O \end{array}$$
 
$$\begin{array}{c} CH_3 \\ \hline \\ \end{array}$$
 
$$\begin{array}{c} CH_3 \\ \hline \\ \end{array}$$

10. Me 
$$\xrightarrow{\text{Me}}$$
  $\xrightarrow{\text{Me}}$   $\xrightarrow{$ 

11. Strength of Nucleophile generally increases on going down a group in the periodic table, so (D) is not true.

12. 
$$CH_2OH$$

$$OCH_3$$

13. Ph-O-CH<sub>2</sub>-CH<sub>2</sub>-OH 
$$\xrightarrow{H^{\oplus}}$$
 Ph-O-CH<sub>2</sub>- $\overset{\oplus}{C}$ H<sub>2</sub>  $\longrightarrow$  Ph-O-CH-CH<sub>3</sub>  $\xrightarrow{Br}$  Ph-O-CH-CH<sub>4</sub>  $\xrightarrow{Br}$  P

14. Nucleophiles are electron rich species.

15. 
$$CH_{3} - C - CH_{2} \leftarrow CH_{3}OH - CH_{3} - C - CH_{2} \leftarrow CH_{3}OH - CH_{3} - C - CH_{2} \leftarrow CH_{3}OH - CH_{3$$

16. 
$$CH_{3} - CH - CH_{2} \xrightarrow{CH_{3}-C^{\circ}C^{-}} CH_{3} - CH - CH_{2} - C \equiv C - CH_{3} \xrightarrow{CH_{3}I} CH_{3} - CH - CH_{2} - C \equiv C - CH_{3}$$

$$OCH_{3} = CH - CH_{2} - C \equiv C - CH_{3} \xrightarrow{CH_{3}I} CH_{3} - CH - CH_{2} - C \equiv C - CH_{3}$$

$$OCH_{3} = [Y]$$

22. S-1 is true and S-2 is **false**.

The transition state for the anti-periplanar arrangement is a staggered conformation, with the base far away from the leaving group. In most cases, this transition state is **lower** in energy than that for the syn-periplanar elimination.

- 23.  $S_N^2$  is not possible at 3° alkyl halide by strong base.
- **24.** Alcohol give S<sub>N</sub> reaction only in acidic medium.
- 25. Polar aprotic solvent is used for  $S_N^2$  reaction because they do not solvate the anion appreciable
- 26. By going top to bottom in periodic table nucleophilicity increases (in protic solvent) because polarisability increases and Iodide is weakly solvated in a protic solvent.

27. 
$$CH_{3} - CH - CH - CH_{3} \xrightarrow{H^{\oplus}} CH_{3} - CH - CH_{3} \xrightarrow{\oplus} CH_{3} - CH_{3} - CH_{3} \xrightarrow{\oplus} CH_{3} - CH_{2} - CH_{3}$$

$$CD_{3} \qquad CD_{3} \qquad CD_{3} \qquad CD_{3}$$

$$CH_{3} - C = CH - CH_{3} + CH_{3} - \overset{*}{CH} - CH = CH_{2} + CH_{2} = C - CH_{2} - CH_{3} + CH_{3} - C - CH_{2} - CH_{3}$$

$$CD_{3} \qquad CD_{3} \qquad CD_{3} \qquad CD_{2}$$
(cis-trans)
$$(d+\ell)$$

- 30.  $-1^{\circ}$  Alkyl halide and anionic strong nucleophile  $\Rightarrow$  S<sub>N</sub>2
  - $-2^{\circ}$  Alkyl halide and anionic strong base  $\Rightarrow E^2$
  - $-3^{\circ}$  Alcohol and acidic medium  $\Rightarrow$  E<sup>1</sup>
  - $-3^{\circ}$  Alkyl halide and weak neutral nucleophile  $\Rightarrow$  S<sub>N</sub>1