Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives X as the major product. Reaction of X with Hg(OAc)₂ / H₂O followed by NaBH₄ gives Y as the major product. Y is (2019 Main, 12 April II)



- **3.** The major product *Y* in the following reaction is (2019 Main, 10 April II)



4. The major product of the following reaction is CH_3



 $\begin{tabular}{ll} \begin{tabular}{ll} $\textbf{5.}$ Which of the following potential energy (PE) diagrams represents the S_N1 reaction? (2019 Main, 9 April II) \\ \end{tabular} \end{tabular} \end{tabular}$



6. The major product of the following reaction is

$$H_{3}C \longrightarrow C \xrightarrow{\text{CH}_{2}CH_{3}} C \xrightarrow{\text{NaOEt}} C \xrightarrow{\text{NaOEt}} C \xrightarrow{\text{OOCH}_{2}CH_{3}} C \xrightarrow{\text{OOCH}_{2}CH_{3}}$$

(2019 Main, 12 Jan II)

(a)
$$CH_3 CH_2 C = CH_2$$

 $CO_2 CH_2 CH_3$
(b) $CO_2 CH_2 CH_3$
 $CH_3 C = CHCH_3$
(c) $H_3 C - C - OCH_2 CH_3$
(d) $H_3 CH_2 C - C - CO_2 CH_2 CH_3$
 $CH_3 C - CO_2 CH_2 CH_3$

7. The major product in the following conversion is

CH₃O — CH — CH — CH₃
$$\xrightarrow{\text{HBr (excess)}}_{\text{Heat}}$$
?
(2019 Main, 12 Jan II)



8. The major product of the following reaction is

$$\begin{array}{c} \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{CH} & \operatorname{CH}_{2} & \xrightarrow{\text{(i) KOH alc.}} \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

9. The major product of the following reaction is



10. Which hydrogen in compound (*E*) is easily replaceable during bromination reaction in presence of light?

 $\begin{array}{ccc} CH_3 {-\!\!\!-} CH_2 {-\!\!\!-} CH {=\!\!\!-} CH_2 & \mbox{(2019 Main, 10 Jan I)} \\ \delta & \gamma & \beta_{(E)} & \alpha \end{array}$

(a) β -hydrogen (b) δ -hydrogen (c) γ -hydrogen (d) α -hydrogen

11. The major product of the following reaction is



12. The major product of the following reaction is



13. The major product of the following reaction is



14. The increasing order of reactivity of the following halides for the S_N1 reaction is (2017 Main)
I. CH₃CH(Cl)CH₂CH₃
II. CH₃CH₂CH₂Cl
III. *p*-H₃CO— C₆H₄— CH₂Cl

(a) (III)
$$<$$
 (I) $<$ (I)
(b) (II) $<$ (I) $<$ (III)

- (c) (I) < (III) < (III)
- (d) (II) < (III) < (II)
- 15. Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ? (2017 Main)



16. 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is (2017 Main)

(a) six
(b) zero
(c) two
(d) four

17. The major product obtained in the following reaction is

$$C_6H_5$$
 $\xrightarrow{Br} C_6H_5 \xrightarrow{t_{BuOK}}$

(2017 Main)

(a) (\pm) C₆H₅CH(O^tBu)CH₂C₆H₅ (b) $C_6 H_5 CH = CHC_6 H_5$ (c) (+) $C_6H_5CH(O^tBu)CH_2C_6H_5$

$$(d) (-)C_6H_5CH(O^tBu)CH_2C_6H_5$$

18. 2-chloro-2-methylpentane on reaction sodium with methoxide in methanol yields (2016 Main)



(a) Both I and III (c) Both I and II

19. The product of the reaction given below is (2015 Adv.)

(d) All of these



20. The synthesis of alkyl fluorides is best accomplished by (2015 Main)

(a) free radical fluorination (b) Sandmeyer's reaction (d) Swarts reaction (c) Finkelstein reaction

21. In $S_N 2$ reactions, the correct order of reactivity for the following compounds CH₃Cl, CH₃CH₂Cl, (CH₃)₂CHCl and (CH₃)₃CCl is (2014 Main) (a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(b) $CH_3Cl > CH_3CH_2 Cl > (CH_3)_2 CHCl > (CH_3)_3 CCl$ (c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$ (d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

22. KI in acetone, undergoes $S_N 2$ reaction with each P, Q, R and S. The rates of the reaction vary as (2013 Adv.)



23. The major product of the following reaction is (2008, 3M)



24. The following compound on hydrolysis in aqueous acetone will give (2005, 1M)



(b) $C_2H_5OC_2H_5$

(d) C_6H_5I

(a) C₆H₅OC₂H₅ (c) $C_6H_5OC_6H_5$ (2003, 1M)

26. Identify the set of reagents/reaction conditions *X* and *Y* in the following set of transformations- (2002, 3M)

$$CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2}Br \xrightarrow{\chi} Product \xrightarrow{Y} CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3}$$

- (a) X = dilute aqueous NaOH, 20°C, Y = HBr/acetic acid, 20°C
- (b) X = concentrated alcoholic NaOH, 80°C,
- $Y = HBr/acetic acid, 20^{\circ}C$
- (c) X = dilute aqueous NaOH, 20°C, $Y = \text{Br}_2/\text{CHCl}_3, 0^{\circ}\text{C}$
- (d) X = concentrated aqueous NaOH, 80°C, $Y = \text{Br}_2/\text{CHCl}_3, 0^{\circ}\text{C}$
- **27.** The compound that will react most readily with NaOH to form methanol is (2001, 1M) (a) $(CH_3)_4 N^+ I^-$ (b) $CH_3 OCH_3$ (c) $(CH_3)_3 S^+ I^-$ (d) $(CH_3)_3 Cl$
- 28. An S_N 2 reaction at an asymmetric carbon of a compound always gives (2001)
 (a) an enantiomer of the substrate
 (b) a product with opposite optical rotation
 (c) a mixture of diastereomers
 (d) a single stereoisomer
- **29.** The order of reactivities of the following alkyl halides for a $S_N 2$ reaction is— (2000, 1M) (a) RF > RCl > RBr > RI (b) RF > RBr > RCl > RI
 - (c) RCl > RBr > RF > RI (d) RI > RBr > RCl > RF
- **30.** Which of the following has the highest nucleophilicity? (2000)

(a)
$$F^{-}$$
 (b) OH^{-} (c) CH_{3}^{-} (d) NH_{2}^{-}

- 31. A solution of (+)-2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of SbCl₅, due to the formation of (1999)
 (a) carbanion (b) carbene
 (c) free-radical (d) carbocation
- 32. Which of the following is an organometallic compound?
 (a) Lithium methoxide
 (b) Lithium acetate
 (c) Lithium dimethylamide
 (d) Methyl lithium
- **33.** (CH₃)₃ CMgCl on treatment with D₂O produces (1997, 1M) (a) (CH₃)₃CD (b) (CH₃)₃COD (c) (CD)₃CD (d) (CD)₃COD
- 34. 1-chlorobutane on reaction with alcoholic potash gives
 (a) 1-butene
 (b) 1-butanol
 (1991, 1M)
 (c) 2-butene
 (d) 2-butanol
- **35.** *n*-propyl bromide on treatment with ethanolic potassium hydroxide produces (1987, 1M) (a) propane (b) propene (c) propyne (d) propanol
- The reaction condition leading to the best yield of C₂H₅Cl are- (1986, 1M)

(a)
$$C_2H_6(excess) + Cl_2 \xrightarrow{UV \text{ light}}$$

(b) $C_2H_6 + Cl_2 (excess) \xrightarrow{dark}_{room \text{ temp.}}$
(c) $C_2H_6 + Cl_2 (excess) \xrightarrow{UV \text{ light}}$
(d) $C_2H_6 + Cl_2 \xrightarrow{UV \text{ light}}$

Objective Questions II

(One or more than one correct option)

37. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are)



(a) Compound IV undergoes inversion of configuration (b) The order of reactivity for I, III and IV is : IV > I > III(c) I and III follow $S_N I$ mechanism (d) I and II follow $S_N I$ mechanism

38. Compound(s) that on hydrogenation produce(s) optically inactive compound (s) is/are (2015 Adv.)



39. In the following reaction, the major product is (2015 Adv.) CH_3



40. The compounds used as refrigerant are (1990, 1M) (a) NH_3 (b) CCl_4 (c) CF_4 (d) CF_2Cl_2 (e) CH_2F_2

Assertion and Reason

41. An **Assertion** and a **Reason** are given below. Choose the correct answer from the following options.

Assertion (A) Vinyl halides do not undergo nucleophilic substitution easily.

Reason (R) Even though the intermediate carbocation is stabilised by loosely held π -electrons, the cleavage is difficult because of strong bonding. (2019 Main, 12 April II) (a) Both (A) and (R) are wrong statements.

- (b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).
- (c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).
- (d) (A) is a correct statement but (R) is a wrong statement.

Match the Columns

42. List-I contains reactions and List-II contains major products.



Match each reaction in List-I with one or more products in List-II and choose the correct option. (2018 Adv.) (a) $P \rightarrow 1, 5; Q \rightarrow 2; R \rightarrow 3; S \rightarrow 4$ (b) $P \rightarrow 1, 4; Q \rightarrow 2; R \rightarrow 4; S \rightarrow 3$

- (c) $P \rightarrow 1, 4; Q \rightarrow 1, 2; R \rightarrow 3, 4; S \rightarrow 4$
- (d) P \rightarrow 4, 5; Q \rightarrow 4; R \rightarrow 4; S \rightarrow 3,4
- **43.** Match the chemical conversion in Column I with the appropriate reagents in Column II and select the correct answer using the code given below the lists. (2013 Adv.)

Column I						Column II
Р.	\rightarrow	Cl			1.	(i) Hg(OAc) ₂ ; (ii) NaBH ₄
Q.	\rightarrow	-ONa ——	\rightarrow)Et	2.	NaOEt
R.		<u>}</u>	»	× ^{OH}	3.	Et-Br
S.			*	ОН	4.	(i) BH ₃ ; (ii)H ₂ O ₂ / NaOH
Co	des					
	Р	Q	R	S		
(a)	2	3	1	4		
(b)	3	2	1	4		
(d)	2	2	4	1		
()	-	-	-	-		

Mate	ch the following :	(2006, 3M)			
	Column I		Column II		
A.	CH_3 — $CHBr$ — CD_3 on treatment with alc. KOH gives CH_2 = CH — CD_3 as a major product.	p.	E1 reaction		
В.	Ph—CHBr—CH ₃ reacts faster than Ph—CHBr—CD ₃	q.	E2 reaction		
C.	Ph— CH_2 — CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph— CD = CH_2 as the major product.	r.	E1CB reaction		
D.	PhCH ₂ CH ₂ Br and PhCD ₂ CH ₂ Br react with same rate.	s.	First order reaction		

Fill in the Blanks

- **45.** Vinyl chloride on reaction with the dimethyl copper gives (1997)
- **46.** The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with (1983, 1M)
- 47. The halogen which is most reactive in the halogenation of alkanes under sunlight is ... (1981, 1M)

True/False

- 48. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1. (1993, 1M)
- **49.** During S_N 1 reactions, the leaving group leaves the molecule before the incoming group is attached to the molecule.

(1990, 2M)

- The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markownikoff's rule. (1989, 2M)
- **51.** Iodide is better nucleophile than bromide. (1985)
- **52.** Carbon tetrachloride is inflammable. (1985, 1/2M)
- Carbon tetrachloride burns in air when lighted to give phosgene. (1983, 1M)

Integer Answer Type Question

54. In the following monobromination reaction, the number of possible chiral product(s) is (are)...

$$H \xrightarrow{CH_2CH_2CH_3} Br \xrightarrow{Br_2(1.0 \text{ mole})}_{300^{\circ}C}$$

$$CH_3$$
(1.0 mole) (Enantiometrically pure)

55. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is

(2011)

Subjective Questions

56. Identify *X*, *Y* and *Z* in the following synthetic scheme and write their structures

$$CH_{3}CH_{2}C \equiv CH \xrightarrow{(i) \text{ NaNH}_{2}} X$$

$$X \xrightarrow{H_{2}/Pd-BaSO_{4}} Y \xrightarrow{alkaline} KMnO_{4} Z$$
(2002, 5M)

57. What would be the major product in each of the following reactions?

(i)
$$CH_3 \xrightarrow[]{CH_3} CH_2Br \xrightarrow[]{C_2H_5OH}{\Delta}$$
 (2000, 2M)

58. Write the structures of the products :

$$C_6H_5CH_2CHClC_6H_5 \xrightarrow{Alc. KOH}$$
 (1998, 2M)

59. Which of the following is the correct method for synthesising methyl-*t*-butyl ether and why?

or
$$(CH_3)_3 CBr + NaOMe \longrightarrow$$

 $CH_3Br + NaO - t - Bu \longrightarrow$ (1997, 2M)

60. Predict the structure of the product in the following reaction

$$\begin{array}{c|c} & Br \\ H & & \\ H & & \\ MeO & & \\ & H \end{array} \xrightarrow{Ph} H \xrightarrow{NaI} acetone \end{array}$$
(1996, 1M)

61. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. (1995, 2M)

62. Draw the stereochemical structure of product in the following reaction

$$Br \xrightarrow{CH_3} H \xrightarrow{NaOH} S_N 2 \xrightarrow{(1994)}$$

- **63.** Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. (1994, 2M)
- 64. Identify the major product in the following reaction.

$$C_6H_5$$
— CH_2 — H_2 — CH_3 $\xrightarrow{Alc. KOH}{\Delta}$? \xrightarrow{HBr} ? (1993, 1M)
Br

65. Write the structures of the major organic product expected from each of the following reactions :

(i)
$$H_3C \xrightarrow{CH_3} CH_2CH_3 \xrightarrow{Alc. KOH} Cl$$

(ii) $CH_3CH_2CHCl_2 \xrightarrow{aq. alkali} boil$ (1992, 2M)

- 66. Arrange the following in order of their
 - (i) Increasing basicity $H_2O, OH^-, CH_3OH, CH_3O^-$
 - $(ii) \ \mbox{Increasing reactivity in nucleophilic substitution reactions} \\ CH_3F, CH_3I, CH_3Br, CH_3Cl \mbox{(1992, 2M)}$
- **67.** Chloroform is stored in dark coloured bottles. Explain in not more than two sentences. (1980, 1M)
- **68.** Show by chemical equations only, how would you prepare the following from the indicated starting materials? Specify the reagents in each step of the synthesis. (1979, 2M)
 - (i) Chloroform from carbon disulphide.
 - (ii) Hexachloroethane (C_2Cl_6) from calcium carbide.

Answers

1.	(c)	2.	(d)	3.	(b)	4. (c)	33.	(a)	34.	(a)	35.	(b)	36.	(a)
5.	(b)	6.	(b)	7.	(d)	8. (d)	37.	(a, d)	38.	(b,d)	39.	(d)	40.	(a,d)
9.	(c)	10.	(c)	11.	(d)	12. (d)	41.	(c)	42.	(b)	43.	(a)		
13.	(b)	14.	(b)	15.	(a)	16. (d)	44.	$A \rightarrow q, B \rightarrow$	q, C	\rightarrow r, D \rightarrow	p, s			
17.	(b)	18.	(d)	19.	(a)	20. (d)	45.	propene	46.	ethyne	47.	chlorine	48.	False
21.	(b)	22.	(b)	23.	(a)	24. (a)	49.	True	50.	True	51.	True	52.	False
25.	(a)	26.	(b)	27.	(a)	28. (d)	53.	False	54.	(5)	55.	(5)		
29.	(d)	30.	(c)	31.	(d)	32. (d)								

Hints & Solutions

1. Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives 1-phenyl but-1-ene(*X*).

Reaction of X with $Hg(OAc)_2 / H_2O$ followed by $NaBH_4$ gives 1-phenyl butan-1-ol (Y). Reaction involved is as follows:

 (Υ)

Ph 1. Hg (OAc)₂,H₂O H_2 O $H_$

2. NaBH₁

Mechanism



 (CH₃)₃CCl gives a precipitate with AgNO₃ solution because it forms stable carbocation. (i.e. tertiary) that readily combines with AgNO₃ to give precipitates of AgCl.

$$CH_{3} \xrightarrow{|} CH_{3} \xrightarrow{|} CH_{$$

 $CH_2 = CH$ —Cl forms unstable carbocation. Hence, it does not readily react with AgNO₃. **3.** The given reaction takes place as follows :



4. In the given question, the substrate is a 2°-halide (bromide) and the medium, CH_3OH (as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly $S_N 1$ pathways *via* the formation of a carbocation intermediate (I).



The intermediate, I can be rearranged into the more stable form I' (3°) by α -hydride shift. I ' will give the major product.



5. The potential energy (PE) diagram for $S_N 1$ reaction is



 $S_N 1$ reaction has two steps. In the first step, the carbon halogen bond breaks heterolytically, with the halogen retaining the previously shared pair of electron. In the second step, the nucleophile reacts rapidly with the carbocation formed in the first step.

In the above graph, the alkyl halide is the only species that participates in the rate limiting step. Here, the rate of reaction depends on the concentration of the alkyl halide and does not depend on the concentration of nucleophile.

6. Presence of strong base (EtO⁻) and heat indicates elimination. Thus, the compound undergo dehydrohalogenation and alkene is produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:

(i)
$$CH_3CH_2C = CH_2$$

 $| COOCH_2CH_3$
(ii) $CH_3CH = C - CH_3$
 $| COOCH_3CH_2$

In accordance with Saytzeff rule

$$CH_3CH = C - CH_3$$
 will be the major product
COOCH₄CH₃

- **7.** Key Idea The excess of HBr and high temperature in given reaction serves for dual purpose:
 - (i) Hydrolysis of ether via $S_N 2$ mechanism, i.e. Zeisel's method.
 - (ii) Markownikoff addition at double bond of the branch.

The road map of complete reaction is as follows:



Here, BB = Bond breakage BF = Bonf formation

8. Key Idea Both alc. KOH and NaNH₂ in liquid NH₃ are dehydrohalogenating reagents. On comparative terms NaNH₂/liquid NH₃ is stronger in action.

The reaction proceeds as :

Thus, option (d) is the correct answer.

9. The given reactant in presence of Cl₂/CCl₄, given *vicinal* dihalide. Chlorine adds up to alkene *via* electrophilic addition reaction involving cyclic chlorinium ion formation.



The vicinal dihalide in presence of anhyd. $AlCl_3$ results in the formation of carbocation that rearranges itself to form a cyclic compound.



10. The compound (*E*) has two allyl-hydrogen atoms (γ). When *E* reacts with Br₂ / $h\nu$, it readily undergoes allylic free radical substitution and forms 3, 3-dibromobut-1-ene

 $\overset{\delta}{\mathrm{C}}$

$$H_{3} \xrightarrow{\gamma} H_{2} \xrightarrow{P} CH = \overset{\alpha}{C} H_{2} \xrightarrow{Br_{2}/h\nu}_{-HBr}$$

$$Br$$

$$CH_{3} \xrightarrow{\downarrow} CH \xrightarrow{P} CH = CH_{2} \xrightarrow{HBr}_{\alpha} \xrightarrow{Br_{2}/h\nu}_{-HBr}$$

$$3 \cdot bromo \cdot but \cdot 1 \cdot ene$$

$$Br$$

$$CH_{3} \xrightarrow{\downarrow} CH \xrightarrow{P} CH$$

3,3- dibromobut-1-ene

11. The reaction follows α , β -elimination mechanism to give a more substituted stable alkene as a major product. As the substrate is a α , γ -dibromo (1, 3-) compound it gives a conjugated diene.



12. In the given reaction, $AlCl_3$ act as Lewis acid and helps in generation of carbocation. The resulting carbocation (1°) rearranges itself to stable carbocation (3°).



13. Complete reaction can be represented as



Thus, the given reaction is dehydrohalogenation which is a β -elimination proceeding through E_2 mechanism.

Mechanism The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H atoms.



- 14. (i) The rate of S_N reaction depends only upon the concentration of the alkyl halide.
 - (ii) S $_{\rm N}$ l reaction proceeds through the formation of carbocation. The reactivity is decided by ease of dissociation of alkyl halide.

$$R \longrightarrow X \Longrightarrow R^{\oplus} + X^{\ominus}$$

Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N 1 reaction.

 $p - H_3CO - C_6H_4 - CH_2^{\oplus}$ is the most stable carbocation due to resonance and then $CH_3 CHCH_2CH_3$ (2° carbocation) while $CH_3CH_2CH_2(1^\circ)$ is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the $S_{\rm N}1$ reaction is

$$\begin{array}{c} \mathrm{CH_3CH_2CH_2Cl} < \mathrm{CH_3CHCH_2CH_3} < p\text{-}\mathrm{H_3COC_6H_4CH_2Cl} \\ | \\ \mathrm{Cl} \\ \mathrm{(II)} & \mathrm{(II)} \end{array} (\mathrm{III)} \end{array}$$

15. To show decolourisation, compound must be unsaturated.



16. The number of stereoisomers in molecules which are not divisible into two equal halves and have *n* number of asymmetric C-atoms = 2^n .

3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e. 2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible



17. An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 (β -elimination reaction).



18. Key Idea Strong nucleophile (OMe) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.

$$CH_{3} \xrightarrow{C} CH_{2}CH_{2}CH_{2}CH_{3} \xrightarrow{MeONa} CH_{3} \xrightarrow{C} CH_{2}-CH_{2}-CH_{2}-CH_{3} \xrightarrow{HeONa} CH_{3} \xrightarrow{C} CH_{2}-CH_{2}-CH_{2}-CH_{3} \xrightarrow{HeONa} CH_{3} \xrightarrow{C} CH_{$$



20. Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

Methyl fluoride

But, when aciton of NaI/acetone takes place on alkyl chloride of bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'

$$C_2H_5Cl \xrightarrow{\text{NaI}} C_2H_5I + \text{NaCl}$$

Free redical fluorination is highly explosive reaction, so not preferred for the preparation of fluoride.

21. Steric hindrance (crowding) is the basis of $S_N 2$ reaction, by using which we can arrange the reactant in correct order of their reactivity towards $S_N 2$ reaction.

Rate of
$$S_N 2 \propto \frac{1}{\text{Steric crowding of 'C'}}$$

 $CH_3Cl > CH_3CH_2Cl > CH_3 - CH - Cl > CH_3 - CH_1 - Cl = CH_2 - Cl$
 $(Less 1^\circ - CH_3 -$

As steric hinderance (crowding) increases, rate of S $_{\rm N}2$ reaction decreases.

Note The order of reactivity towards $\mathrm{S}_{\!N}^{}2$ reaction for alkyl halides is

$$\begin{array}{l} \text{Primary}\\ \text{halides} \\ (1^{\circ}) \\ \end{array} > \begin{array}{l} \text{Secondary}\\ \text{halides} \\ \text{halides} \\ (2^{\circ}) \\ \end{array} > \begin{array}{l} \text{Tertiary}\\ \text{halides} \\ \text{halides} \\ (3^{\circ}) \end{array}$$

 $\begin{array}{cccc} \textbf{22. PLAN} & \text{Acetone is an aprotic solvent and can dissolve both the} & & & \text{nucleophile and the substrate and thus } S_N^2 \text{ reaction is favoured.} & & & \text{Also} & & & \\ & & & S_N^2 \xleftarrow{1^\circ} & 2^\circ & 3^\circ & & \\ & & & \text{Alkyl halides} & & & \end{array}$

$$S_{N2} \xrightarrow{1^{\circ} 2^{\circ} 3^{\circ}} Alkyl halides$$

$$S_{N1}$$
S.
$$O = I^{\circ} alkyl halide but (C-Cl).$$
B.E. is decreased by electron withdrawing [C₆H₅CO] group, (a case of *I*-effect). Thus, maximum rate in S_N 2 reaction
Q.
$$Cl = I^{\circ} alkyl halide$$
R.
$$Cl = I^{\circ} alkyl halide$$
R.
$$Cl = I^{\circ} alkyl halide$$
I alkyl halide but allylic 1° carbocation is resonance stabilised in S_N 1 reaction

Thus, reactivity order is S > P > R > Q

23. Nucleophile PhS⁻ substitute the Br⁻ through $S_N 2$ mechanism wih inversion of configuration at α -C.



24. Reaction proceed through carbocation intermediate



Lack of β -H on quaternary ammonium iodide leads to $S_N 2$ reaction otherwise E2 elimination usually takes place.

- **28.** $S_N 2$ reaction at asymmetric carbon occur with inversion of configuration and a single steroisomer is formed because the reactant and product are not enthtiomer. Therefore the sign of optical rotation may or may not change.
- **29.** If alkyl groups are same, the order of leaving ability of halides in $S_N 2$ reaction is

30. CH_3^- , being the strongest base, has highest nucleophilicity.

31.
$$C_6H_5 \longrightarrow \stackrel{l}{\underset{H}{\overset{} \subset}} CH_3 + SbCl_5 \rightleftharpoons C_6H_5 \longrightarrow \stackrel{l}{\underset{H}{\overset{} \subset}} CH_3 + SbCl_6^-T$$

he planar carbocation (I), when return back, forms racemic mixture of the starting compounds.

32. Compound in which metal is directly bonded to carbon, is known are organometallic compound, e.g. CH₃Li.

33.
$$CH_3 \xrightarrow[C]{H_3} D_2O \xrightarrow[C]{H_3} CH_3$$

 $H_3 \xrightarrow[C]{-} MgCl^+ \xrightarrow[D_2O]{H_3} CH_3 \xrightarrow[C]{-} D$
 $H_3 \xrightarrow[C]{H_3} CH_3$

34.
$$CH_3 - CH_2 - CH_2 - CH_2 - CI + KOH \xrightarrow{C_2H_3OH} CH_3CH_2 - CH = CH_2$$

I-butene

35. An alkyl halide containing at least one β -H, on treatment with ethanolic KOH, undergoes dehydrohalogenation, giving alkene.

alkene. CH₃—CH₂—CH₂—Br + KOH $\xrightarrow{\text{Ethanol}}$ CH₃—CH=CH₂

36. During chlorination of alkane, if excess of alkane is treated with $Cl_2(g)$ in presence of light or heat, chance of mono-chlorination predominate.

$$C_2H_6 (excess) + Cl_2 \xrightarrow{UV-light} CH_3CH_2Cl + HCl$$

- 37. (a) Both I and II are 1° halide, undergos S_N2 reaction.
 (d) III is a tertiary halide, undergoes S_N2 reaction. I is benzylic bromide, it is very reactive in S_N1 also as if produces stable benzylic carbonation.
- **38.** In both cases, hydrogenation of olefinic bond will render compound achiral as two identical ethyl group will come at the α -carbon which was earlier chiral carbon. However, in (*a*) and (*c*), chirality will be retained even after hydrogenation.



39. Since, there is no mention of temperature, room temperature will be considered and thermodynamically controlled product would be the major product as:



- **40.** Both NH_3 and CF_2Cl_2 are used as refrigerant.
- **41.** Vinyl halide (CH₂=CH—Cl) do not undergo nucleophilic substitution reactions. This is because it forms highly unstable carbocation (CH₂= $\stackrel{\oplus}{C}$ H). It cannot delocalise its π -electron. In vinyl halide C—Cl bond possess double bond character also.

$$\dot{CH_2}$$
 CH $\dot{CH_2}$ CH $\dot{CH_2}$ $-CH$ $=$ $\ddot{CH_2}$ $\dot{CH_2}$ $-CH$ $=$ $\ddot{CH_2}$ $\dot{CH_2}$ $\dot{CH$

42. For P, i.e.
$$\overline{ONa}^+ + Br$$

For this reaction 1 and 4 are probable products.

Product 1 i.e., \rightarrow_{OH} is formed due to substitution while product 4 i.e., \downarrow_{H} is formed due to elimination. A tertiary carbocation i.e, \downarrow_{H} formed during the reaction. Remember for 3° carbocation ions elimination product predominates.

Correctly matched product for this reaction is 2 i.e., The reaction proceeds as

$$\bigvee_{OMe}$$
 + HBr \rightarrow MeOH + \bigvee_{Br}

For
$$R$$
 i.e., $+$ NaOMe

Correctly matched product is 4 i.e., . It is a normal elimination reaction and proceeds as

$$+ \overset{+-}{\operatorname{NaOMe}}_{\operatorname{Br}} \xrightarrow{} \overset{+-}{\operatorname{Alkali in}}_{\operatorname{alcohol}} \xrightarrow{} \overset{+-}{\operatorname{Alkali in}}$$

3° alkyl halide preferes elimination.

For S i.e.,
$$+$$
 MeB

The correct match is 3 i.e., OMe . The reaction proceeds as

$$h_{\text{DNa}}^+$$
 + MeBr \longrightarrow + NaBr
OMe

43.

	Column I	Column II	Explanation
P.	\rightarrow cl \rightarrow	NaOEt(2)	O Et (strong nucleophile) causes dehydrohalogenation of 3° alkyl halide
Q.	\rightarrow ONa \rightarrow \rightarrow OEt	EtBr(3)	3° butoxide undergoes $S^{}_N$ reaction with 1° alkyl halide



nus,
$$P - (2)$$
, $Q - (3)$, $R - (1)$, $S - (4)$

44. A.
$$CH_3$$
— $CHBr$ — $CD_3 \xrightarrow{Alc. KOH} CH_2 = CH$ — CD_3

E2 reaction is a single-step reaction in which both deprotonation from β -C and loss of leaving group from α -C occur simultaneously in the rate-determining step.

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C-D bond is stronger than C—H bond, C—H is preferably broken in elimination.

B. Ph—CHBr—CH₃ reacts faster than Ph—CHBr—CD₃ in E2 reaction because in latter case, stronger C-D bond is to be broken in the rate determining step.

C. Ph—CH₂—CH₂Br
$$\xrightarrow{C_2H_5OD}$$
 Ph—CD=CH₂

Deuterium incorporation in the product indicates E1CB mechanism C II O-

$$Ph - CH_{2} - CH_{2}Br \xrightarrow{C_{2}H_{5}O} Ph - \overline{CH} - CH_{2}Br$$

$$\xrightarrow{C_{2}H_{5}OD} Ph - CHD - CHD - CH_{2}Br$$

$$I \xrightarrow{C_{2}H_{5}O^{-}} Ph - \overbrace{C}^{P} - CH_{2} - CH$$

- D. Both PhCH₂CH₂Br and PhCD₂CH₂Br will react at same rate in E1 reaction because C-H bond is broken in fast non rate determining step. Also E1 reaction follow first order kinetics.
- **45.** Propene is produced

 $(CH_3)_2Cu + CH_2 = CHCl \longrightarrow CH_3 - CH = CH_2$

- **46.** Vinyl chloride is obtained by the reaction of HCl with ethyne.
- 47. Chlorine is most reactive.
- **48.** 2-bromo-2-methylpropane is formed as major product.
- 49. In $S_N 1$ reaction, leaving group is detached in the first step forming carbocation intermediate.
- **50.** True
- 51. Larger the size of donor atom, greater is its polarisability, stronger is the nucleophile.
- **52.** False
- **53.** CCl_4 is fire retardent, used as fire-extinguisher.

54. Given compound undergoes free-radical bromination under given conditions, replacing H by Br.

C^{*} is chiral carbon.

II. Achiral



III. Chiral



(III) has two chiral centres and can have two structures.



(IV) has also two chiral centres and can have two structures.



It has plane of symmetry thus, achiral. Thus, chiral compounds are five. I, III A, III B, IV B and V.

55. The substrate has three different types of B—H, therefore, first three structural isomers of alkenes are expected as :



The last two alkenes II and III are also capable of showing geometrical isomerism, hence two geometrical isomers for each of them will be counted giving a total of five isomers.



 C_2H_5 meso-diol

57. Unimolecular reaction occur



58.
$$C_6H_5CH_2$$
— CH — $C_6H_5 \xrightarrow{Alc. KOH} C_6H_5$ — CH = CH — C_6H_5





-н

—н





Above equilibrium is established which has equilibrium constant equal to 1. Therefore, equilibrium mixture will have both the enantiomers in equal amount giving racemic mixture.

62. $S_N 2$ reactions leads to inversion of configuration at α -C

NaOH





-OH

CH₃

Η·



Due to the above resonance phenomena, C - X bond acquire partial double bond character and becomes difficult to break in the rate determining step of S_N^2 reaction.

64.
$$C_{6}H_{5}CH_{2}$$
— CH — $CH_{3} \xrightarrow{Alc. KOH} C_{6}H_{5}$ — $CH = CH$ — CH_{3}
Br
 $\downarrow HBr$
 $C_{6}H_{5}$ — CH — CH_{2} — CH_{3}
Br
 CH_{3}
 $GH_{3}C$ — $CH_{2}CH_{3} \xrightarrow{Alc. KOH} CH_{3}$ — $C= CHCH_{3}$
(ii) $H_{3}C$ — $CH_{2}CHCl_{2} \xrightarrow{Aq. NaOH} [CH_{3}CH_{2}$ — CH — OH]
 $Unstable$
 $-H_{2}O$ $CH_{3}CH_{2}CHC$

- **66.** (i) $H_2O < CH_3OH < HO^- < CH_3O^-$ (ii) $CH_3F < CH_3Cl < CH_3Br < CH_3I$
- 67. Chloroform in presence of air and sunlight, oxidises slowly to form a highly poisonous compound called phosgene

$$2\text{CHCl}_3 + \text{O}_2 \xrightarrow{h\nu} 2\text{COCl}_2 + 2\text{HCl}$$
(Phosgene)

To prevent the above oxidation reaction, chloroform is kept in dark bottles.

68. (i) $CS_2 + Cl_2 \longrightarrow CCl_4 + S_2Cl_2$ $CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$ $CCl_4 + 2[H] \xrightarrow{Fe/H_2O} CHCl_3 + HCl_{(Chloroform)}$ $CaC_2 + H_2O \longrightarrow C_2H_2 + Ca(OH)_2$ (ii)

$$C_2H_2 \xrightarrow{H_2/Ni} C_2H_6 \xrightarrow{Cl_2 (excess)} h_{\nu} \xrightarrow{Cl_3C} CCl_3 (Hexachloroethane)$$