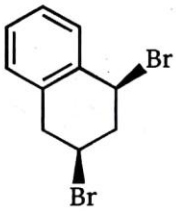
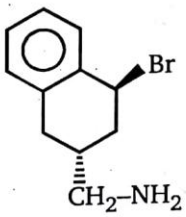
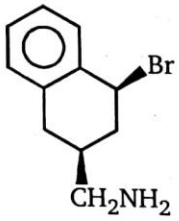
5c ALKYL HALIDES

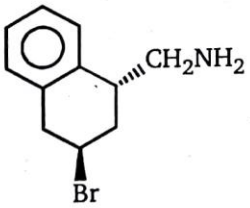
LEVEL-1

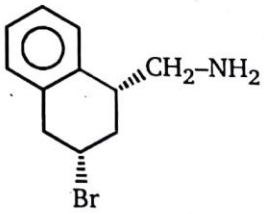
1. 

$\xrightarrow[2\ LiAlH_4]{1.\ \text{One eq. NaCN}}$ (*A*); Product (*A*) is :

(a) 

(b) 

(c) 

(d) 

2. In the reactions given below,

$$R - Cl \xrightarrow{\text{(i) KCN, (ii) } LiAlH_4} \text{Product } A$$

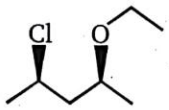
$$R - Cl \xrightarrow{\text{(i) AgCN, (ii) } LiAlH_4} \text{Product } B$$

the compounds A and B are :

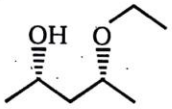
(a) chain isomers (b) position isomers

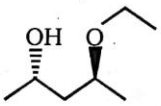
(c) functional isomers (d) metamers

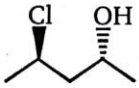
3. Which is the major product expected from the following S_{N^2} reaction ?

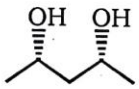


$\xrightarrow{NaOH}$ Product

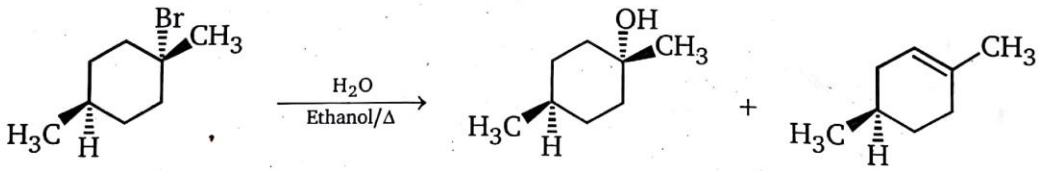
(a) 

(b) 

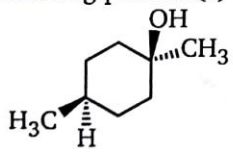
(c) 

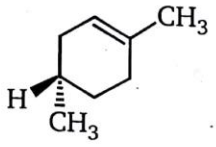
(d) 

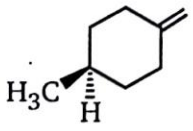
4. Consider the following E_1/S_{N^1} reaction :

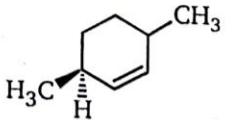


The missing product(s) is(are) :

(1) 

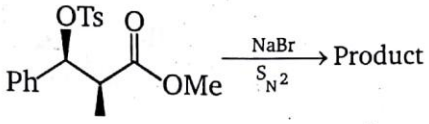
(2) 

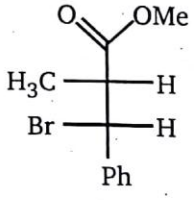
(3) 

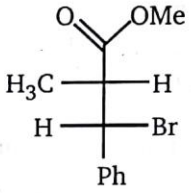
(4) 

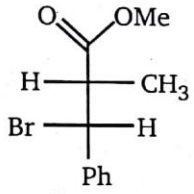
(a) 1, 2 and 3 (b) 3 and 4 (c) 2 and 3 (d) 1, 2, 3 and 4

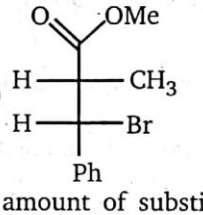
5. What is the product of the following S_{N^2} reaction ?



(a) 

(b) 

(c) 

(d) 

6. Select the reagent that will yield the greater amount of substitution on reaction with CH_3-CH_2-Br :

(a) CH_3CH_2OK in dimethyl sulfoxide (DMSO)

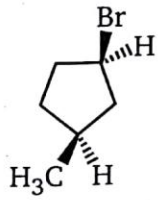
(b) $(CH_3)_3COK$ in dimethyl sulfoxide (DMSO)

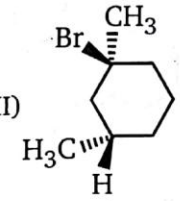
(c) Both (a) and (b) will give comparable amounts of substitution

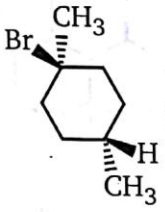
(d) Neither (a) nor (b) will give any amount of substitution

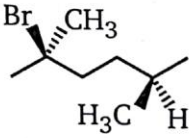
7. Under the specified conditions, substrate X undergoes substitution and elimination reactions to give products $A-D$. A and B are stereoisomers, but not enantiomers. C and D are enantiomers. A is not an isomer of C. Which of the following could be the starting material X ?

$$X \xrightarrow[\Delta]{H_2O} A + B + C + D$$

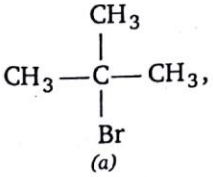
(I) 

(II) 

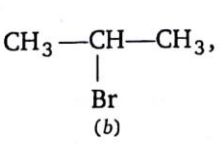
(III) 

(IV) 

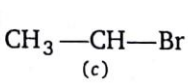
(a) (I) (b) (II) (c) (III) (d) (IV)

8. 

(a)



(b)

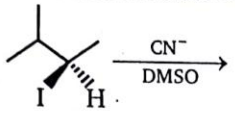


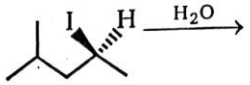
(c)

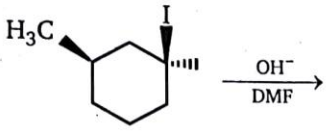
Compare rate of E_2 reaction :

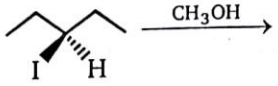
(a) $c > b > a$ (b) $a > b > c$ (c) $b > a > c$ (d) $c > a > b$

9. Which reaction results in the formation of a pair of enantiomers ?

(a) 

(b) 

(c) 

(d) 

10. Rate limiting S_{N^1} follows the sequence

$$\overset{\delta\oplus\ \delta\ominus}{R\text{–Br}} \rightleftharpoons \underset{(a)}{\boxed{R^{\oplus}\,Br^{\ominus}}} \rightleftharpoons \underset{(b)}{\boxed{R^{\oplus}}\ \boxed{Br^{\ominus}}} \rightleftharpoons \boxed{R^{\oplus}} \rightleftharpoons \underset{(c)}{\boxed{Br^{\ominus}}}$$

True statement about sequence on the basis of assumption that *R* contains 3 different groups is :

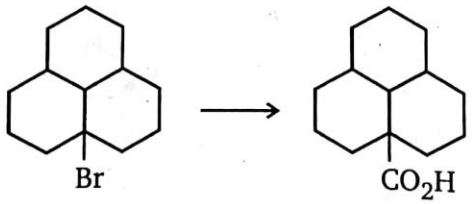
(a) more stable carbocation, greater is in the proportion of racemization
(b) the more nucleophilic the solvent greater in the proportion of inversion
(c) In above sequence (*b*) represent separately solvated, pair of ions
(d) All of these

11. Compare the two methods shown for the preparation of carboxylic acids :

Method 1 : $RBr \xrightarrow[\text{diethyl ether}]{Mg} RMgBr \xrightarrow[2.\,H_3O^+]{1.\,CO_2} RCO_2H$

Method 2 : $RBr \xrightarrow{NaCN} RCN \xrightarrow[\text{heat}]{H_2O,\ HCl} RCO_2H$

Which one of the following statements correctly describes this conversion ?

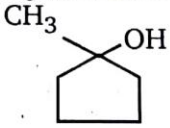
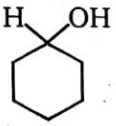


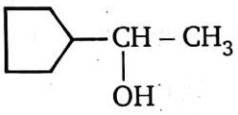
(a) Both method 1 and method 2 are appropriate for carrying out this conversion
(b) Neither method 1 nor method 2 is appropriate for carrying out this conversion
(c) Method 1 will work well, but method 2 is not appropriate
(d) Method 2 will work well, but method 1 is not appropriate

12. Which of the following statements is true ?

(a) $CH_3CH_2S^-$ is both a stronger base and more nucleophilic than $CH_3CH_2O^-$
(b) $CH_3CH_2S^-$ is a stronger base but is less nucleophilic than $CH_3CH_2O^-$
(c) $CH_3CH_2S^-$ is a weaker base but is more nucleophilic than $CH_3CH_2O^-$
(d) $CH_3CH_2S^-$ is both a weaker base and less nucleophilic than $CH_3CH_2O^-$

13. In the given pair of alcohols, in which pair second alcohol is more reactive than first towards hydrogen bromide ?

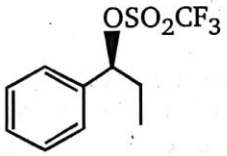
(a)  and 

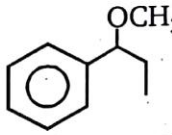
(b)  and 

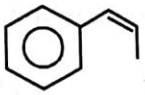
(c) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$ and $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$

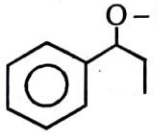
(d) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$ and $(CH_3)_2\underset{\underset{OH}{|}}{C}-CH_2-CH_3$

14. Which product would be expected to predominate in the given reaction ?



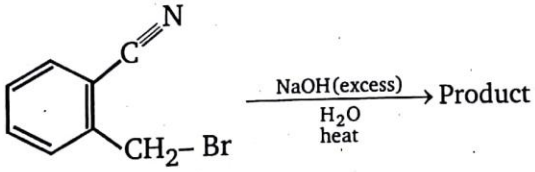
(a) 

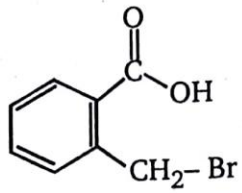
(b) 

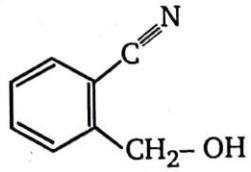
(c) 

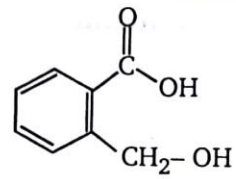
(d) None of these

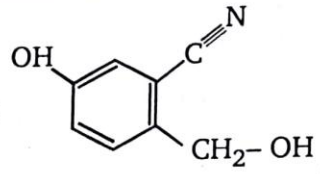
15. Which is the major product of the following reaction ?

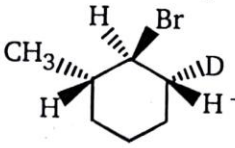


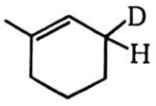
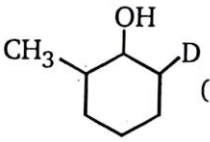
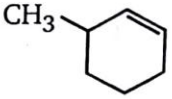
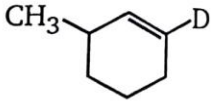
(a) 

(b) 

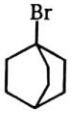
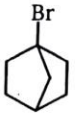
(c) 

(d) 

16.  $\xrightarrow{\text{Alc. KOH}}$ (A) ; Major product of this reaction is :

(a)  (b)  (c)  (d) 

17. Rate of S_{N^2} reaction is :

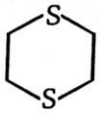
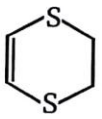
 (A)  (B)  (C)

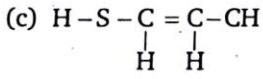
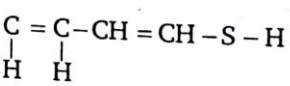
(a) $(B) > (A) > (C)$ (b) $(C) > (A) > (B)$

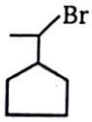
(c) $(A) > (B) > (C)$ (d) $(A) > (C) > (B)$

18. 1-2-dichloro ethane + $NaSCH_2CH_2SNa \longrightarrow C_4H_8S_2 + (P)$

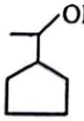
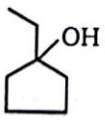
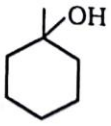
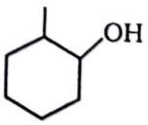
Unknown product (P) of the above reaction is :

(a)  (b) 

(c)  (d) 

19.  $\xrightarrow{\text{Moist } Ag_2O}$ (A) product

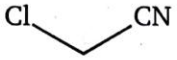
Major product (A) is :

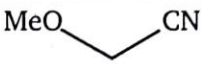
(a)  (b)  (c)  (d) 

20. 

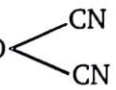
(MOM chloride)
(Methoxy methyl chloride)

$\xrightarrow{KCN}$ Product of reaction is :

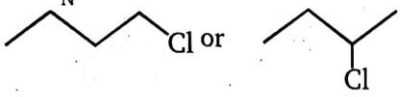
(a) 

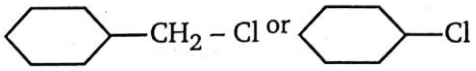
(b) 

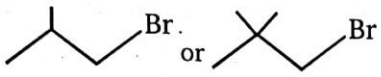
(c) $Me-O-CH_2-CH_2-CN$

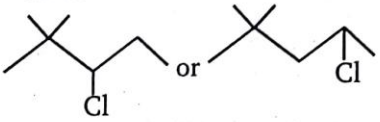
(d) 

21. In the given pair of compound, in which pair the second compound is more reactive than first toward S_{N^2} reaction ?

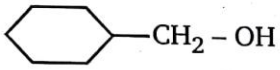
(a) 

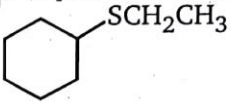
(b) 

(c) 

(d) 

22. Which compound might be synthesized by the S_{N^2} displacement of an alkyl-halide ?

(a) 

(b) 

(c) Me_3C-OCH_3

(d) All of these

23. Identify *C* in the following series $C_3H_7I \xrightarrow[\text{alc.}]{KOH} A \xrightarrow[\Delta]{NBS} B \xrightarrow[\text{alc.}]{KCN} C.$

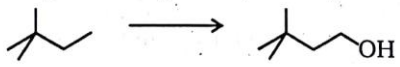
(a) $(CH_3)_2CH-CN$

(b) $CH_2=CH-CH_2CN$

(c) $Br-CH=CH-CN$

(d) $CH_2=CH-\underset{\displaystyle Br}{\underset{|}{C}}HCN$

24. What sequence of reagents is required to accomplish the following transformation ?



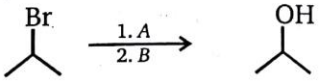
(a) (1) NBS, *R*OOR (2) $CH_3CH_2O^-$ (3) 2HBr (4) NH_2^- (5) disiamyl borane (6) H_2O_2, OH^-

(b) (1) Cl_2 hν (2) OH^-, heat; (3) 2HCl (4) OH^-, heat (5) $HgSO_4$, H_2SO_4

(c) (1) NBS, *R*OOR; OH^-, DMSO

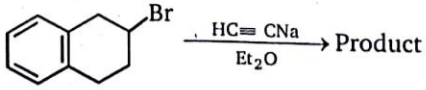
(d) (1) Br_2, hν (2) *t*-butoxide (3) BH_3, THF (4) H_2O_2, OH^-

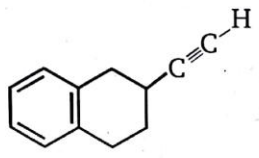
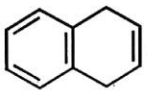
25. Which of the reagents shown below would accomplish the following transformations?

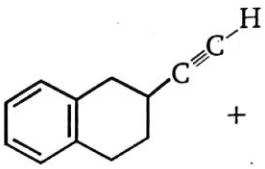
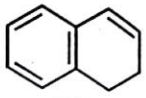


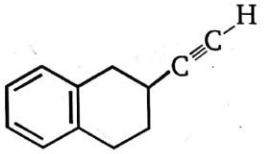
A	*B*
(a) H_3O^+	BH_3 – THF; H_2O_2/NaOH
(b) NaOH	BH_3 – THF; H_2O_2/NaOH
(c) HBr in ether	$Hg(OAc)_2/H_2O$; $NaBH_4$
(d) $NaNH_2$	$Hg(OAc)_2/H_2O$; $NaBH_4$

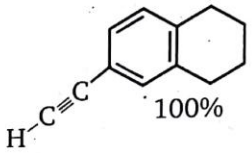
26. What are the products obtained from the following reaction ?



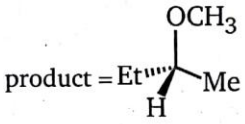
(a)  20% +  80%

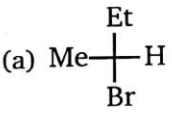
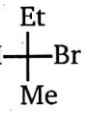
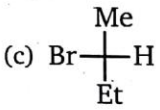
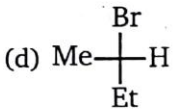
(b)  20% +  80%

(c)  100%

(d)  100%

27. The back-side attack on 2-bromobutane by methoxide (CH_3O^-) gives the product shown below. Which Fischer projection represents 2-bromobutane used as the reactant in this reaction ?



(a)  (b)  (c)  (d) 

28. Consider the following statements :

(1) Bridgehead halides are inert towards both S_{N^1} and S_{N^2} reactions (till one of the ring size is eight member ring)

(2) The first step in both S_{N^1} and E_1 reactions is the same

(3) S_{N^2} reactions proceed with total retention of configuration

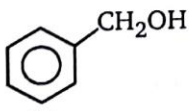
(4) E_2 eliminations are by the use of a solvent of low polarity and high concentration of a strong base

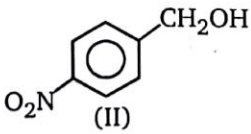
Which of the above statements are correct?

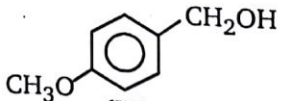
(a) 1, 2 and 4 (b) 1 and 3

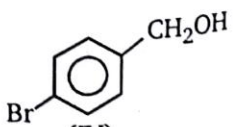
(c) 2, 3 and 4 (d) 1, 2, 3 and 4

29. Consider the following alcohols :

 (I)

 (II)

 (III)

 (IV)

The order of decreasing reactivities of these alcohols towards substitution with HBr is :

(a) III > I > IV > II (b) III > I > II > IV

(c) I > III > IV > II (d) I > III > II > IV

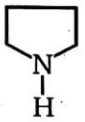
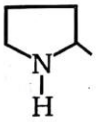
30. In solvolysis of 1,2-dimethyl propyl *p*-toluene sulfonate in acetic acid at 75°C, how many (alkene + substitution) products will be formed ?

(a) 2 (b) 3 (c) 4 (d) 5

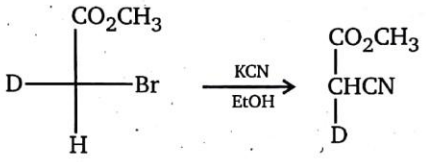
31. Benzotrichloride reacts with milk of lime to form :

(a) Benzal (b) Benzoic acid (c) Benzyl alcohol (d) Phenol

32. $Br-CH_2-(CH_2)_2-CH_2-Br + CH_3NH_2 \longrightarrow$ Product of the reaction is :

(a)  (b)  (c)  (d) 

33. The configurations of the reactant and the product in the following reaction, respectively, are:



(a) R, R (b) R, S (c) S, R (d) S, S

34. 1-4-dichlorohexane (1 mole) + NaI (1 mole) $\xrightarrow{\text{Acetone}}$ Product of the reaction is :

(a) $Cl-CH_2-CH_2-\underset{\displaystyle I}{\underset{|}{CH}}-CH_2-CH_3$ (b) $I-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$

(c) $H_2C=CH-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$ (d) $I-CH_2-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2-CH_3$

35. Alkyl halides can be obtained by all methods except :

(a) $CH_3CH_2OH + HCl/ZnCl_2 \longrightarrow$ (b) $CH_3-CH_2-CH_3-CH_2 \xrightarrow{Cl_2/\text{UV light}}$

(c) $C_2H_5OH + NaCl \longrightarrow$ (d) $CH_3COOAg + Br_2/CCl_4 \longrightarrow$

36. In order to prepare 1-chloropropane, which of the following reactants can be employed ?

(a) Propene and HCl in the presence of peroxide

(b) Propene and Cl_2 followed by treatment with aq. KOH

(c) Propanol-1 and $SOCl_2$/pyridine

(d) Any of the above can be used

37. Which alkyl halide has maximum density ?

(a) C_3H_7I (b) C_2H_5I (c) CH_3I (d) CH_3Br

38. Which of the following molecules would have a carbon-halogen bond most susceptible to nucleophilic substitution ?

(a) 2-fluorobutane (b) 2-chlorobutane

(c) 2-bromobutane (d) 2-iodobutane

39. When benzyl chloride is treated with ethanolic KCN, the major product formed is :
(a) benzyl ethyl ether (b) benzyl alcohol (c) benzyl cyanide (d) benzyl isocyanide

40. Which of the following is most reactive towards nucleophilic substitution reaction ?
(a) $CH_2 = CH - Cl$ (b) C_6H_5Cl
(c) $CH_3CH = CHCl$ (d) $ClCH_2 - CH = CH_2$

41. Which of the following reaction will not give ether as a major product ?
(a) $CH_3CH_2Cl + Ag_2O(dry) \longrightarrow$ (b) $(CH_3)_3CCl + CH_3CH_2O^-Na^+ \longrightarrow$
(c) $CH_3CH_2Cl + Na^+O^-$–C$_6$H$_5$ $\longrightarrow$ (d) $CH_3Cl + Na^+O^- - C(CH_3)_3 \longrightarrow$

42. $O^{\ominus}-S(=O)-O^{\ominus}$ $\xrightarrow{H^+}$ (A), $\xrightarrow{CH_3-I}$ (B)

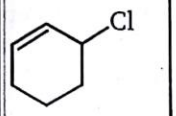
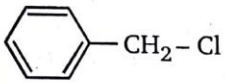
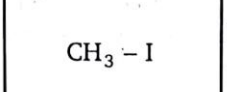
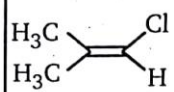
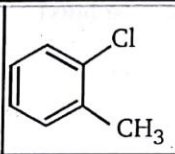
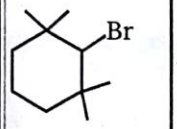
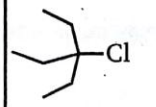
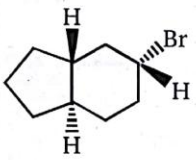
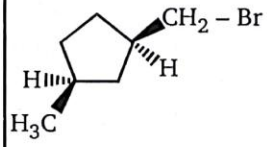
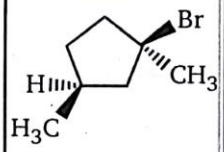
Product (A) and (B) in above reaction is :
(a) $O^- - S(=O) - O - H, O^- - S(=O) - O - CH_3$ (b) $O^- - S(=O) - O - H, O^- - \overset{\oplus}{S}(=O)(O^-) - CH_3$
(c) $O^- - S(=O) - O - CH_3, O^{\ominus} - \overset{\oplus}{S}(=O)(CH_3) - H$ (d) $O^- - \overset{\oplus}{S}(=O)(H) - O, O^- - S(=O)(CH_3) - O^-$

ANSWERS — LEVEL 1															
1.	(c)	**2.**	(c)	**3.**	(b)	**4.**	(a)	**5.**	(a)	**6.**	(a)	**7.**	(c)	**8.**	(b)
9.	(b)	**10.**	(d)	**11.**	(c)	**12.**	(c)	**13.**	(d)	**14.**	(a)	**15.**	(c)	**16.**	(c)
17.	(c)	**18.**	(a)	**19.**	(c)	**20.**	(b)	**21.**	(d)	**22.**	(d)	**23.**	(b)	**24.**	(d)
25.	(d)	**26.**	(b)	**27.**	(d)	**28.**	(a)	**29.**	(a)	**30.**	(d)	**31.**	(b)	**32.**	(b)
33.	(d)	**34.**	(d)	**35.**	(c)	**36.**	(c)	**37.**	(a)	**38.**	(d)	**39.**	(c)	**40.**	(d)
41.	(b)	**42.**	(b)												

LEVEL-2

1. The following organic halide derivatives (*A* to *J*) are reacted in ethanol solution with each of the nucleophiles : acetate, methylthiolate, cyanide and hydroxide anions. Six possible results from these combinations of reactants are designated (1) through (6) below :

Write the number corresponding to your best estimate of the outcome of each reaction in the appropriate answer box below.

				
A	*B*	*C*	*D*	*E*
				
F	*G*	*H*	*I*	*J*

Possible Outcome :

(1) No reaction
(2) Substitution
(3) Elimination
(4) Substitution and elimination
(5) No reaction or slow substitution
(6) No reaction or slow elimination

Compound		*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
(i)	CH_3CO_2Na										
(ii)	CH_3SNa										
(iii)	NaCN										
(iv)	NaOH										

2. In each of the following sections three organic halogen compounds are listed. In the box given enter a number (1 to 3) indicating the order of reactivity of the designated (1 is most reactive and 3 is least).

(a) S_{N^2} substitution by $NaOCOCH_3$ in methanol:
1. $CH_3CH_2CH_2Br$ ☐ 2. $(CH_3)_2CHBr$ ☐ 3. $CH_2=CHCH_2Br$ ☐

(b) S_{N^2} substitution by NaI in acetone:
1. C_6H_5Cl ☐ 2. $C_6H_5CH_2Cl$ ☐ 3. $C_6H_5CHClCH_3$ ☐

(c) S_{N^2} substitution by NaCN in methanol:
1. CH_3CH_2Cl ☐ 2. CH_3CH_2F ☐ 3. CH_3CH_2I ☐

(d) S_{N^2} substitution by $NaSCH_3$ in methanol:
1. $(CH_3)_2CHCH_2CH_2Br$☐ 2. $CH_3CH_2CHBrCH_2CH_3$☐ 3. $(CH_3)_3CCH_2Br$ ☐

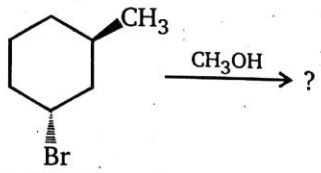
3. Isobutyl alcohol (2-methyl-1-propanol), $(CH_3)_2CHCH_2OH$, can be transformed to each of the compounds (a through l) listed in the left-hand column. In each case the number of steps needed to accomplish the change is noted, and an answer box is provided for your reagent selections. Fourteen reagents (designated A through N) are listed in the right-hand column.

Write letters designating the reagent or reagents you believe will achieve the desired transformation in the box to the right of the product formula. In the case of a multi-step sequence write the reagents in the order they are to be used. In some cases you may wish to use a previously prepared compound as a reactant. If so, write the number (a to l) corresponding to the desired compound.

	Desired product	No. of Steps	Write Options		Reagent List
a.	$(CH_3)_2CHCH_2Br$	one		**A.**	$Hg(OAc)_2$ in H_2O
b.	$(CH_3)_2C=CH_2$	one		**B.**	PBr_3 & heat
c.	$(CH_3)_2CHCH=O$	one		**C.**	$NaBH_4$ in alcohol
d.	$(CH_3)_2CHCO_2H$	one		**D.**	$LiAlH_4$ in THF (aqueous workup)
e.	$(CH_3)_3CBr$	two		**E.**	NaCN in alcohol
f.	$(CH_3)_2CHCH_2C\equiv N$	two		**F.**	PCC in CH_2Cl_2
g.	$(CH_3)_2CHCH_2OCOCH_3$	one		**G.**	Jones' reagent (CrO_3 in H_3O^+)
h.	$(CH_3)_2CHCO_2C_2H_5$	two		**H.**	HBr in CH_2Cl_2
i.	$(CH_3)_2CHCH_2OCH_2(CH_3)$	two		**I.**	H_3PO_4 and heat
j.	$(CH_3)_3COH$	three		**J.**	$(CH_3CO)_2O$ + pyridine
k.	$(CH_3)_2CHCH_2NH_2$	three		**K.**	NaN_3 in aqueous alcohol
l.	$(CH_3)_2CHCH_2CH_2NH_2$	two		**L.**	$C_6H_5CO_3H$ in CH_2Cl_2 (peracid)
				M.	NaH in ether and heat
				N.	C_2H_5OH + acid catalyst & heat

SUBJECTIVE PROBLEMS

1.



X = Total number of substitution and elimination product(s). Find the value of X.

ANSWERS — LEVEL 2

1.	A	B	C	D	E	F	G	H	I	J
(i)	2	2	2	1	1	1	6	2	2	6
(ii)	2	2	2	1	1	5	6	2	2	6
(iii)	2	2	2	1	1	1	3	3	2	3
(iv)	4	2	2	1	1	5	3	3	4	3

2. a – 3 > 1 > 2; b – 2 > 3 > 1; c – 3 > 1 > 2; d – 1 > 2 > 3

3. a – B; b – I; c – F; d – G; e – I, H or 2 H; f – B, E or 1, E; g – J; h – G, N or 4N
i – N, j – I, A, C or 2AC or ILD or 2LD; k – B, K, D or 1KD; l – B, E, D or 1ED or 6D

Subjective Problems

1. 4