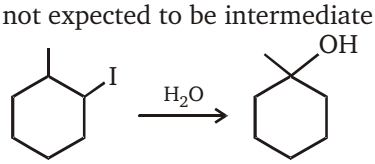
5A

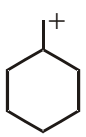
ALKYL HALIDES

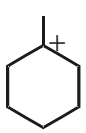
Substitution Reactions (S_{N^1}, S_{N^2}, S_{N^i})

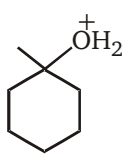
Level - 1

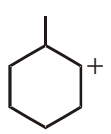
1. Which of the following is not expected to be intermediate of the following reaction ?

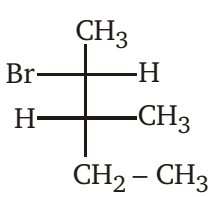


(a) 

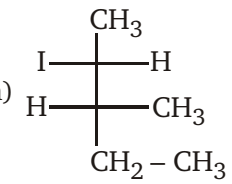
(b) 

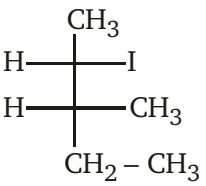
(c) 

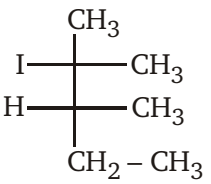
(d) 

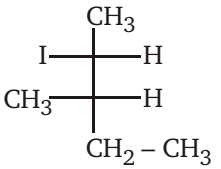
2. 

NaI $\xrightarrow[\text{Acetone}]{}$ product; S_{N^2} product of the reaction is :

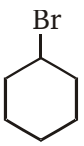
(a) 

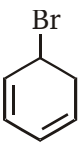
(b) 

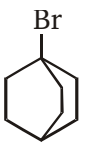
(c) 

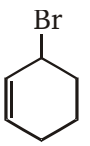
(d) 

3. Rate of S_{N^2} will be negligible in :

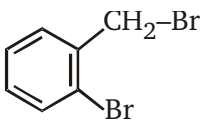
(a) 

(b) 

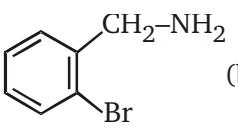
(c) 

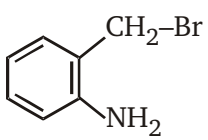
(d) 

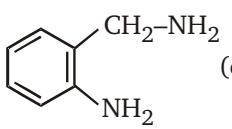
4. What is the major product obtained in the following reaction ?

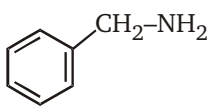


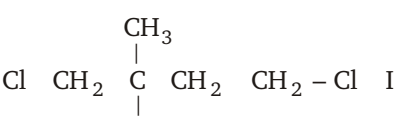
$\xrightarrow[EtOH]{NH_3}$ product

(a) 

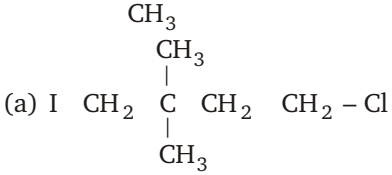
(b) 

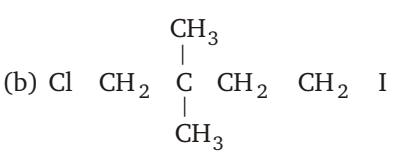
(c) 

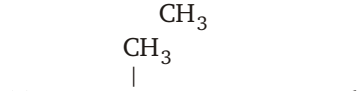
(d) 

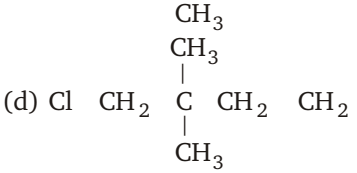
5. 

$\xrightarrow{DMF}$ product; Major product of this reaction is:

(a) 

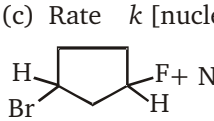
(b) 

(c) 

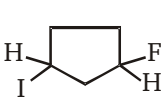
(d) 

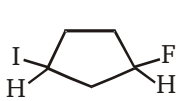
6. Which of the following expressions is representative of the rate law for a S_{N^2} reaction ?

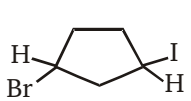
(a) Rate = k [electrophile]
(b) Rate k [electrophile] [nucleophile]
(c) Rate k [nucleophile]^2
(d) Rate k[electrophile]^2

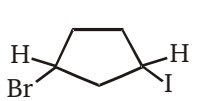
7. 

+ NaI (1 mole) $\xrightarrow{\text{Acetone}}$ (A) ; Major product of this reaction is :
(major)

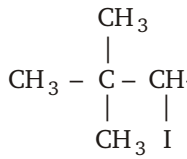
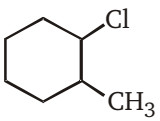
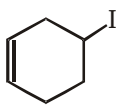
(a) 

(b) 

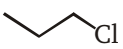
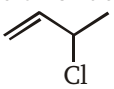
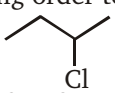
(c) 

(d) 

8. Which of the following alkyl halide undergo rearrangement in S_{N^1} reaction ?

(a)  (b)  (c)  (d) All of these

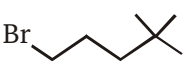
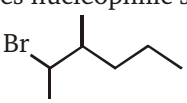
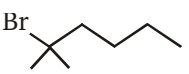
9. Arrange the following three chlorides in decreasing order towards S_{N^1} reactivity.

(1)  (2)  (3) 

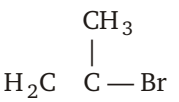
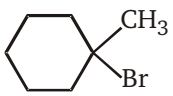
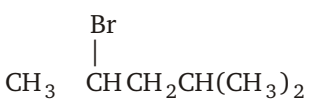
(a) 1 > 2 > 3 (b) 2 > 3 > 1

(c) 2 > 1 > 3 (d) 3 > 2 > 1

10. Which compound undergoes nucleophilic substitution with NaCN at the fastest rate ?

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

11. Rank the following in order of decreasing rate of solvolysis with aqueous ethanol (fastest slowest)

 (1)  (2)  (3)

(a) 2 > 1 > 3 (b) 1 > 2 > 3

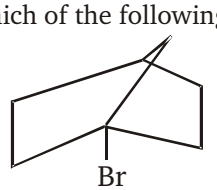
(c) 2 > 3 > 1 (4) 1 > 3 > 2

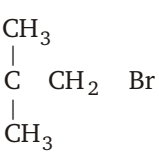
12. The reaction of 4-bromobenzyl chloride with sodium cyanide in ethanol leads to the formation of :

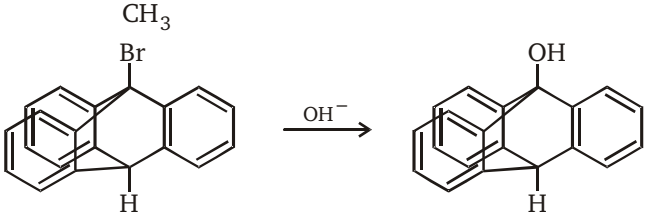
(a) 4-bromobenzyl cyanide (b) 4-cyanobenzyl chloride

(c) 4-cyanobenzyl cyanide (d) 4-bromo-2-cyanobenzyl chloride

13. Which of the following reactant will not favour nucleophilic substitution reaction ?

(a)  (b) Ph Br

(c)  (d) All the above

14. 

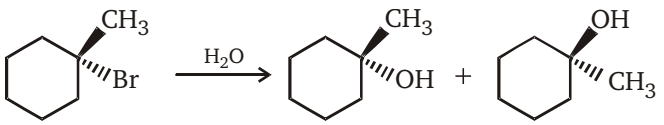
(I) (II)

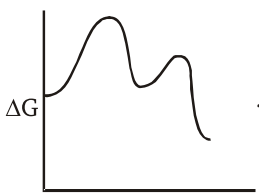
Conversion of I to II :

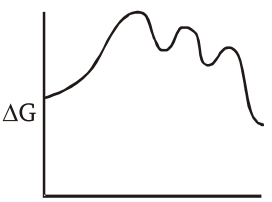
(a) takes place by S_{N^1} (b) takes place by S_{N^2}

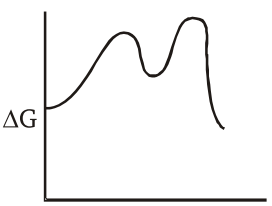
(c) takes place both by S_{N^1} and S_{N^2} (d) does not take place

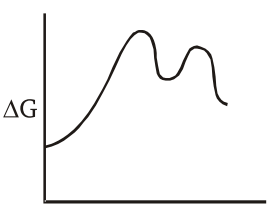
15. Which is the correct reaction coordinate diagram for the following solvolysis reaction ?

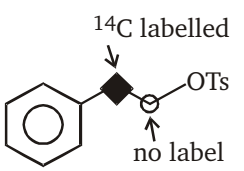


(a)


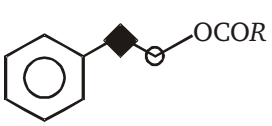
(b)


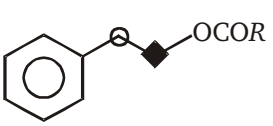
(c)


(d)


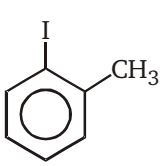
16.


RCO_2H product; Product of this reaction is :

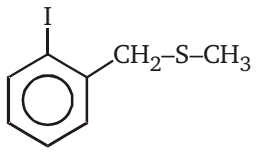
(a)


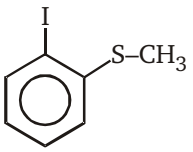
(b)


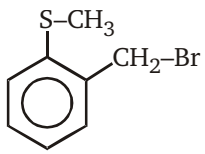
(c) both (a) and (b) (d) None of these

17.


NBS (*A*) CH_3SNa (*B*) , Product (*B*) is :

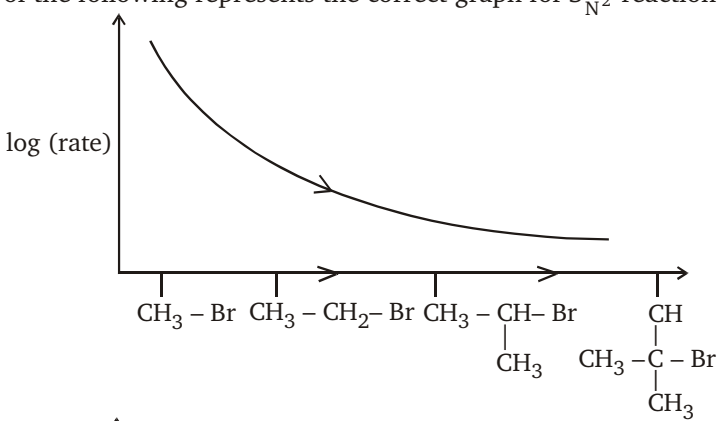
(a) 

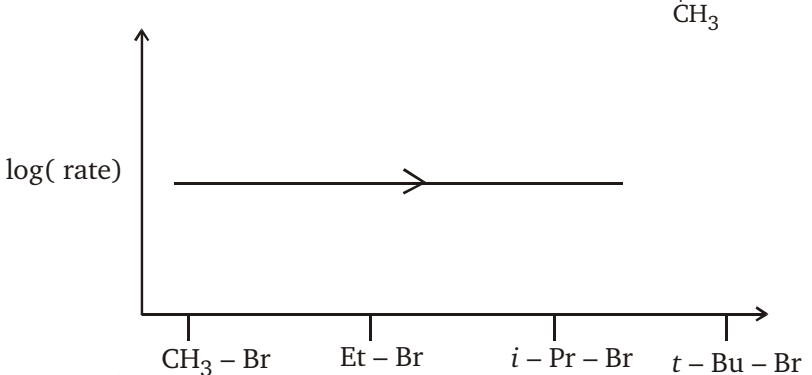
(b) 

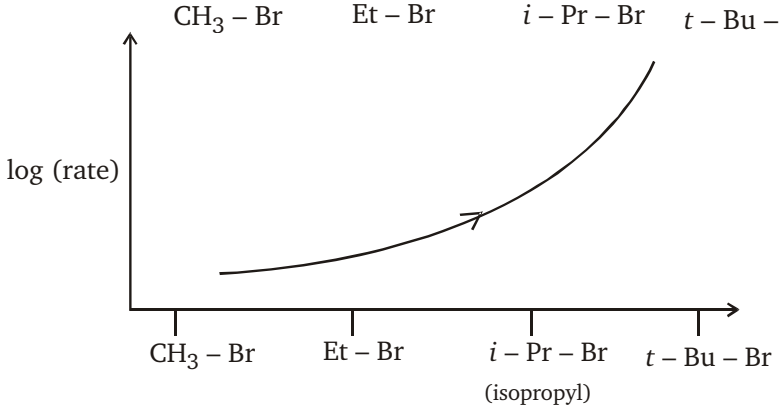
(c) 

(d) None of these

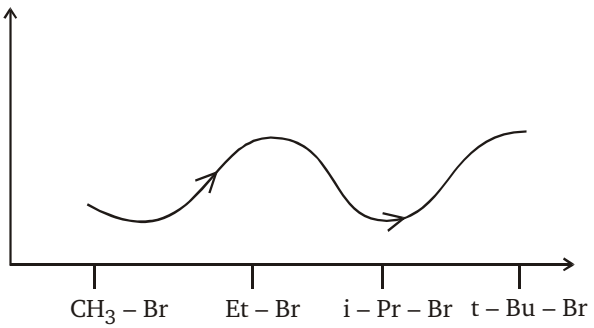
18. Which of the following represents the correct graph for S_{N^2} reaction ?

(a) 

(b) 

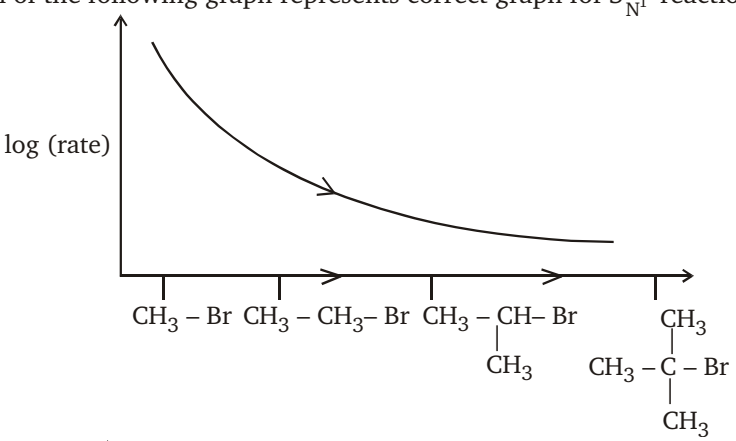
(c) 

(d)

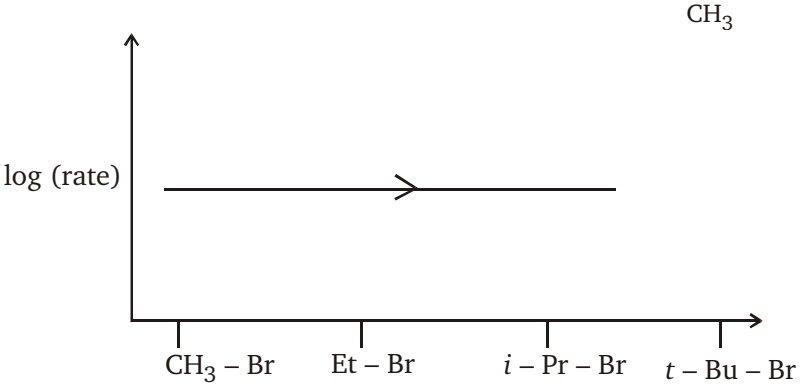


19. Which of the following graph represents correct graph for S_{N^1} reaction :

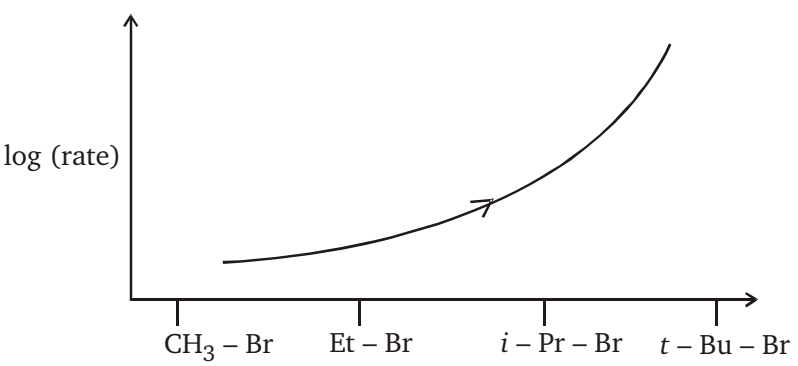
(a)



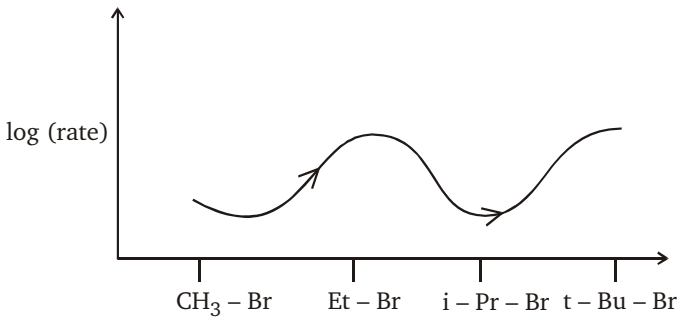
(b)



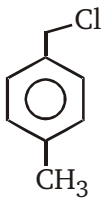
(c)

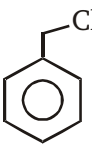


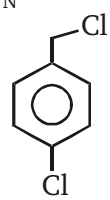
(d)

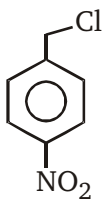


20. Which of the following is most reactive toward S_{N^2} reaction ?

(a) 

(b) 

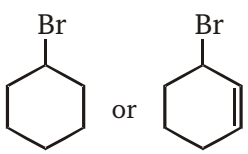
(c) 

(d) 

21. Among the given pairs, in which pair first compound reacts faster than second compound in S_{N^1} reaction ?

(a) $CH_3-CH_2-CH_2-CH_2-Br$ or $CH_3-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$

(b) $CH_3-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_2$ or $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(c) 

(d) $CH_3-\underset{\displaystyle Br}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$ or $CH_3-\underset{\displaystyle I}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$

22. What is the major product of the following reaction ?

$$H_2C-CH-CH_2-OH \xrightarrow[\text{excess}]{HBr} \text{Product}$$

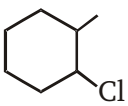
(a) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-Br$

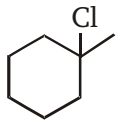
(b) $H_2C-CH-CH_2-Br$ (OH)

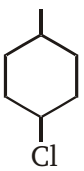
(c) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-OH$

(d) $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-OH$

23. S_{N^1} and S_{N^2} products are same with (excluding stereoisomer) :

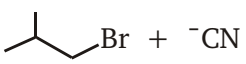
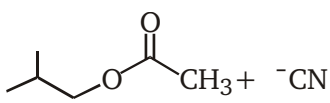
(a) 

(b) 

(c) 

(d) Ph $\underset{\underset{CH_3}{|}}{CH}$ $\underset{\underset{Cl}{|}}{CH}$ CH_3

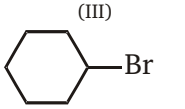
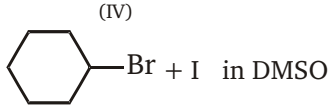
24. Consider the nucleophilic attacks given below. Select in each pair that shows the greater S_{N^2} reaction rate.

(A)  or 

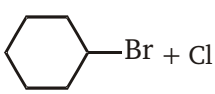
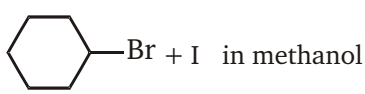
(I) (II)

(B) H_3C Br SH or H_3C Br CH_3SH

(III) (IV)

(C)  or 

(V) (VI)

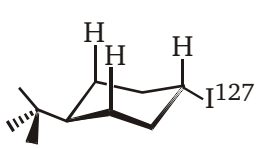
(D)  or 

(VII) (VIII)

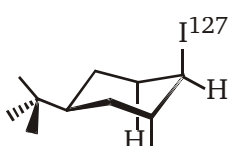
	A	B	C	D
(a)	(I) ;	(IV) ;	(VI) ;	(VIII)
(c)	(I) ;	(III) ;	(V) ;	(VIII)

	A	B	C	D
(b)	(II) ;	(III) ;	(V) ;	(VIII)
(d)	(I) ;	(III) ;	(V) ;	(VII)

25. Which of the two stereoisomers of 4-*t*-butylcyclohexyl iodide (^{127}I) will undergo S_{N^2} substitution with ^{128}I faster, and why ?



(*A*)



(*B*)

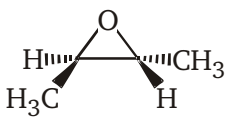
(a) *A* will react faster because it is the more stable of the two isomers

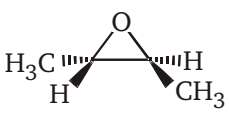
(b) *A* will react faster because it will yield a more stable product, and the transition state for both reactions is of the same energy

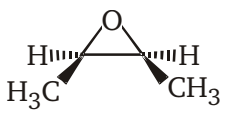
(c) *A* will react faster because the approach of ^{128}I can depart unhindered.

(d) *B* will react faster because it is less stable than *A*, and the transition state for both reactions is of the same energy

26. (*Z*)-2-Butene reacts with Br_2/H_2O. The resulting bromohydrin when treated with methoxide in methanol undergoes an intramolecular S_{N^2} reaction. Taking into consideration the stereochemical consequences of the reaction mechanism involved, choose the final product(s) of these transformations.

(I) 

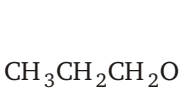
(II) 

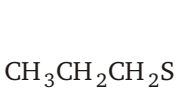
(III) 

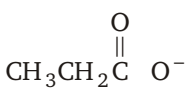
(a) (I) only (b) (II) only

(c) (III) only (d) Equal amounts of (I) and (II)

27. Rank the following species in order of decreasing nucleophilicity in a polar protic solvent (most least nucleophilic) :

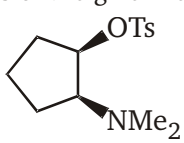

(1)

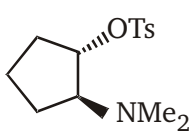

(2)

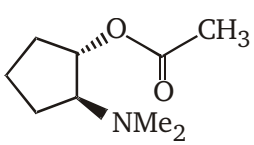
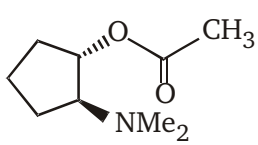

(3)

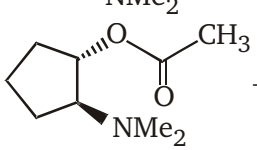
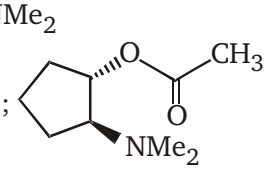
(a) 3 1 2 (b) 2 3 1 (c) 1 3 2 (d) 2 1 3

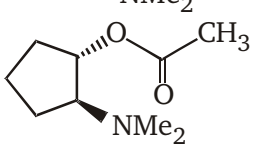
28. Identify products of the given reactions :

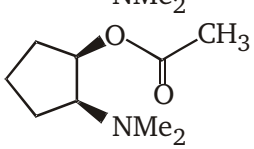
Reaction-1  CH_3CO_2Na / CH_3CO_2H Product

Reaction-2  CH_3CO_2Na / CH_3CO_2H Product

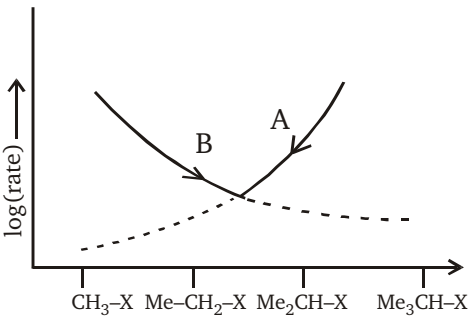
(a)  ;  + enantiomer

(b)  + enantiomer ; 

(c)  single product is obtained in both the reactions

(d)  single product obtained in both the reactions

29.

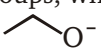


Which of the following is true about given graphs *A* and *B* ?

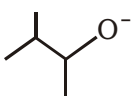
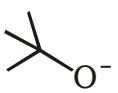
(a) *A* S_{N^1} *B* S_{N^2} (b) *A* S_{N^2}, *B* S_{N^1}

(c) *A* & *B* E_1 (d) *A* & *B* E_2

30. In each of the following groups, which is the strongest (best) nucleophile ?

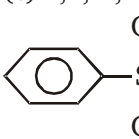
(I) (1) H_3C O (2)  (3) H_3 C S in CH_3OH

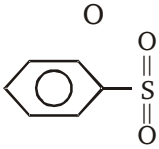
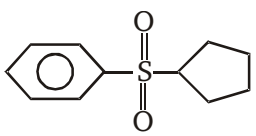
(II) (1) OH (2) H_2O (3) NH_2 in DMF

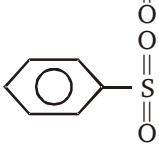
(III) (1)  (2)  (3) CH_3O in DMSO

(a) I,3 ; II,3 ; III,2 (b) I,2 ; II,1 ; III,3

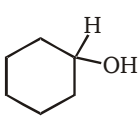
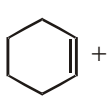
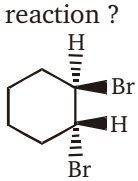
(c) I,1; II,2 ; III,1 (d) I,3 ; II,1 ; III,3

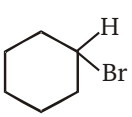
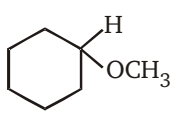
31.  $\xrightarrow[\text{dimethoxy ethane}]{NaNH_2}$ (*A*) ; Product (*A*) is : (Major)

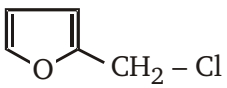
(a)  (b) 

(c)  (d) None of these

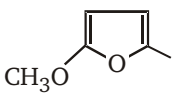
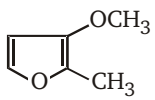
32. Which of the following reaction is an elimination reaction ?

(a)  $\xrightarrow{H_2SO_4}$  + H (b)  $\xrightarrow{KI}$  + IBr + KBr

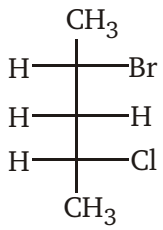
(c)  $\xrightarrow{NaOCH_3}$  (d) both (a) and (b)

33.  $\xrightarrow[CH_3OH(S_{N1})]{CH_3ONa}$ Product

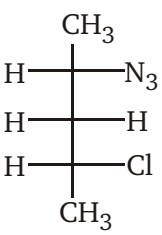
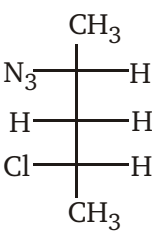
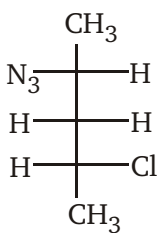
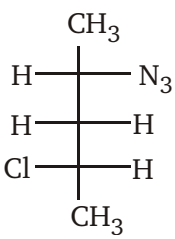
Which of the following products can be obtained from above reaction ?

(a)  (b)  (c)  (d) All of these

34. What is the principal product of the following reaction ?



NaN_3 Product

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

35. What would be the effect of increasing solvent polarity on the rate of each of the following reactions ? (Nu neutral nucleophile)

(A) Nu *R* *L* Nu *R* *L*

(a) increases (b) decreases (c) constant (d) can not be predicted

(B) *R* *L* *R* :*L*

(a) increases (b) decreases (c) constant (d) cannot predict

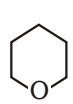
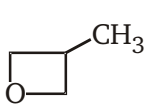
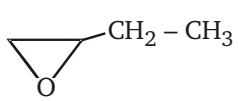
36. Which of the following is most reactive toward S_{N^2} reaction ?

(a) CH_2 CH CH_2 Cl (b) Ph CH_2 Cl

(c) Me – O Cl (d) Ph C CH_2 Cl (O)

37. 4-chloro-1-butanol + NaOH (*B*)

Product (*B*) of the above reaction is :

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

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

(a) $(CH_3)_2CHBr$ or $CH_3\ CH_2\ CH_2\ Br$

(b) $CH_3\ CH_2\ CH_2\ Br$ or $CH_3\ CH_2\ CH_2\ I$

(c) $Ph\ Br$ or $CH_3\ CH_2\ CH_2\ Br$

(d) $CH_2\ CH\ CH_2\ Cl$ or $H_2C\ CH\ Cl$

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

(a) $CH_3\ CH_2\ Cl\ CH_3\ CH_2\ O^-$ $\quad Et\ O\ Et$ (or)

$CH_2\ CH_2\ Cl\ CH_3\ CH_2\ OH$ $\quad Et\ O\ Et$

(b) $CH_3\ CH_2\ Cl\ EtO$ $\quad Et\ O\ Et$ (or)

$CH_3\ CH_2\ Cl\ EtS^-$ $\quad CH_3\ CH_2\ S\ Et$

(c) $\underset{(1m)}{Et}\ Cl\ \underset{(2m)}{CH_3O}$ $\quad Et\ O\ CH_3$ (or)

$\underset{(2m)}{Et}\ Cl\ \underset{(1m)}{CH_3O}$ $\quad Et\ O\ CH_3$

(d) $Et\ Br\ Ph_3P$ $\quad Et\ PPh_3$ (or)

$Et\ Br\ Ph_3N$ $\quad E\ NPh_3$

40. Among the following pair of reactions in which pair the second reaction is more reactive than first in S_{N^1} reaction ?

(a) $Me_3CCl\ H_2O$ $\quad Me_3COH$ $\quad$ (or) $\quad Me_3CBr\ H_2O$ $\quad Me_3COH$

(b) $Me_3CCl\ CH_3OH$ $\quad Me_3C-OCH_3$ (or) $Me_3C-Cl + H_2O \rightarrow Me_3C-OH$

(c) $\underset{(1M)}{Me_3CCl}\ H_2O$ $\quad$ (or) $\quad \underset{(2M)}{Me_3CCl}\ H_2O$

(d) All of these

41. Which is a true statement concerning the transition state of an S_{N^2} reaction ?

(a) Closely resembles a carbocation intermediate

(b) The electrophile is responsible for the reaction

(c) Lower is energy than the starting materials

(d) Involves both the nucleophile and electrophile

42. Increasing the concentration of a nucleophile in a typical S_{N^2} reaction by a factor of 10 will cause the reaction rate to :

(a) increase by a factor of 10 (b) increase by a factor of 10^2

(c) decrease by a factor of 10 (d) remain about the same

43. Decreasing the concentration of an electrophile in a typical S_{N^2} reaction by a factor of 3 will cause the reaction ratio to :

(a) increase by a factor of 3 (b) increase by a factor of 3^2

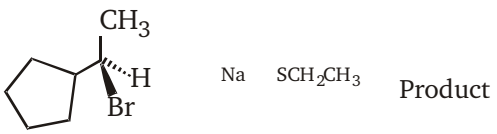
(c) decrease by a factor of 3 (d) remain about the same

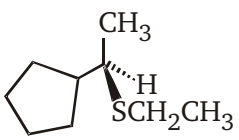
44. Increasing the concentration of an electrophile in a typical S_{N^2} reaction by a factor of 3 and the concentration of the nucleophile by a factor of 3 will change the reaction rate to :

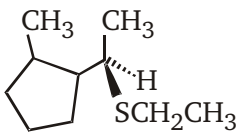
(a) increase by a factor of 6 (b) increase by a factor of 9

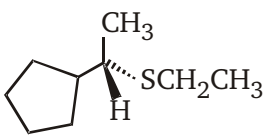
(c) decrease by a factor of 3 (d) remain about the same

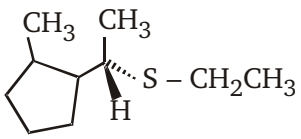
45. Consider the following reaction and select the best choice that represents the reaction.

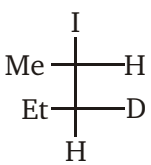


(a) 

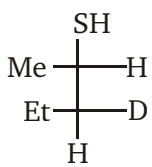
(b) 

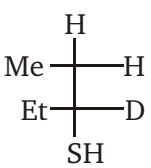
(c) 

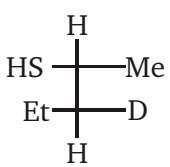
(d) 

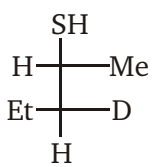
46. 

KSH Product; Identify the product.

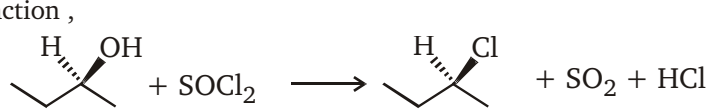
(a) 

(b) 

(c) 

(d) 

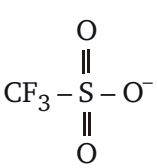
47. The reaction ,



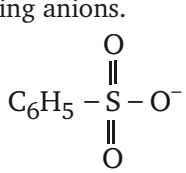
proceeds by the..... mechanism.

(a) S_{N^i} (b) S_{N^2} (c) S_{E^2} (d) S_{N^1}

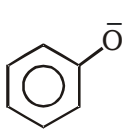
48. Consider the following anions.



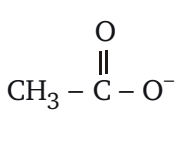
(I)



(II)



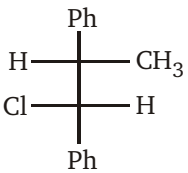
(III)



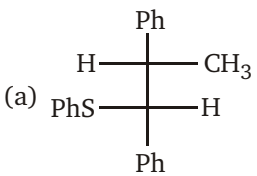
(IV)

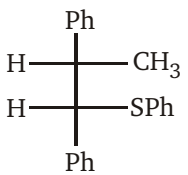
When attached to sp^3-hybridized carbon, their leaving group ability in nucleophilic substitution reaction decreases in the order :

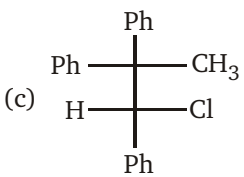
(a) I > II > III > IV (b) I > II > IV > III (c) IV > I > II > III (d) IV > III > II > I

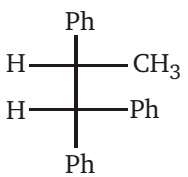
49. 

Principal organic product of the reaction will be :

(a) 

(b) 

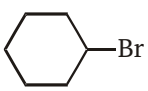
(c) 

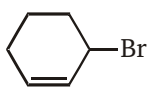
(d) 

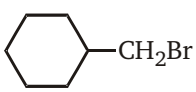
50. Reaction of *R*-2-butanol with *p*-toluenesulphonyl chloride in pyridine followed by reaction with LiBr gives:

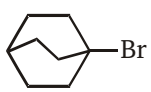
(a) *R*-2-butyl bromide
(b) *S*-2-butyl tosylate
(c) *R*-2-butyl tosylate
(d) *S*-2-butyl bromide

51. The compound which undergoes S_{N^1} reaction most rapidly is :

(a) 

(b) 

(c) 

(d) 

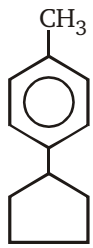
52. Addition of KI accelerates the hydrolysis of primary alkyl halides because :

(a) KI is soluble in organic solvents
(b) the iodide ion is a weak base and a poor leaving group
(c) the iodide ion is a strong base
(d) the iodide ion is a powerful nucleophile as well as a good leaving group

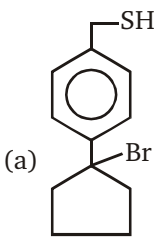
53. Which of the following phrases are not correctly associated with S_{N^1} reaction ?

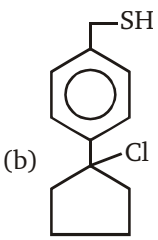
(1) Rearrangement is possible
(2) Rate is affected by polarity of solvent
(3) The strength of the nucleophile is important in determining rate
(4) The reactivity series is tertiary > secondary > primary
(5) Proceeds with complete inversion of configuration

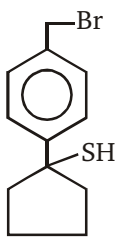
(a) 3, 5
(b) 5 only
(c) 2, 3, 5
(d) 3 only

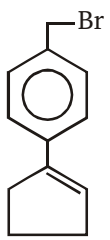
54. 

$\xrightarrow[h\nu]{SO_2Cl_2}$ (*A*) $\xrightarrow{NBS}$ (*B*) $\xrightarrow{KSH}$ (*C*) , Product (*C*) is :

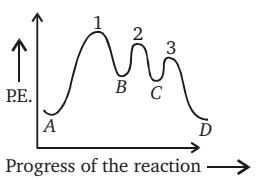
(a) 

(b) 

(c) 

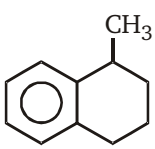
(d) 

55. Energy profile diagram for an exothermic reaction, *A* $\xrightarrow{1}$ *B* $\xrightarrow{2}$ *C* $\xrightarrow{3}$ *D*, is given below.



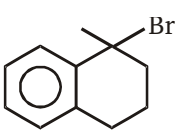
The rate determining step of the reaction is :

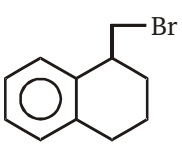
(a) *A* *B* (b) *B* *C* (c) *C* *D* (d) can not predict

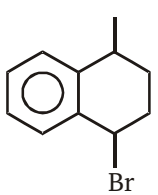
56. 

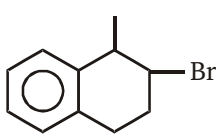
$\xrightarrow{NBS}$ (*A*) Major

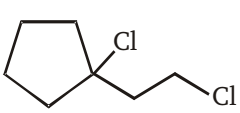
Major product (*A*) is :

(a) 

(b) 

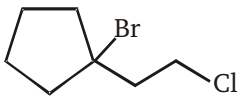
(c) 

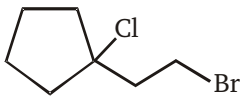
(d) 

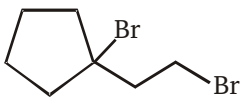
57. 

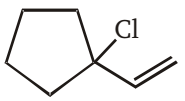
$\xrightarrow[S_{N}2 \text{ conditions}]{LiBr/DMSO}$ Major product (*X*)

The product *X* is :

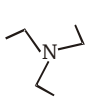
(a) 

(b) 

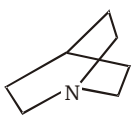
(c) 

(d) 

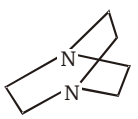
58. Relative rate of reaction of the following amine with methyl iodide is:



(A)

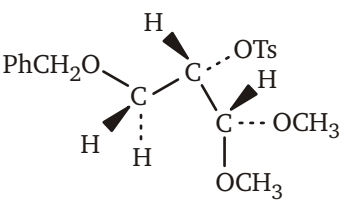


(B)



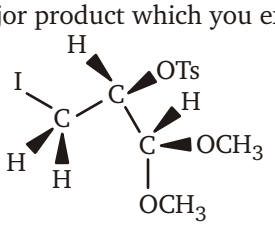
(C)

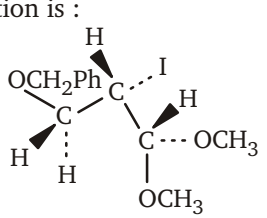
(a) A > B > C (b) A > C > B (c) B > C > A (d) B > A > C

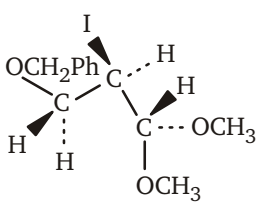
59. 

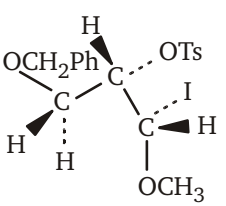
NaI
Dimethyl sulfoxide

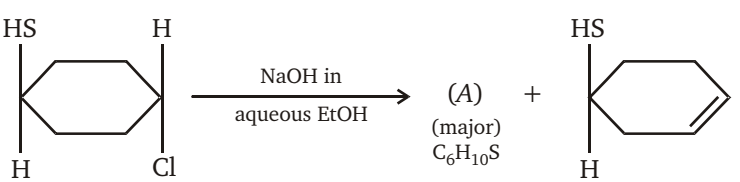
Major product which you expect in the above reaction is :

(a) 

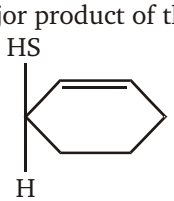
(b) 

(c) 

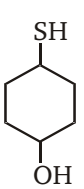
(d) 

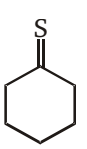
60. 

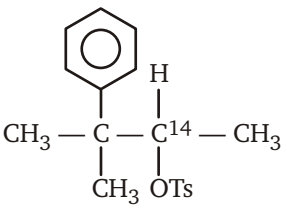
Major product of the above reaction is :

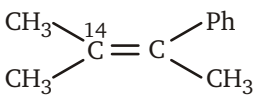
(a) 

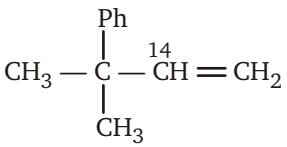
(b) 

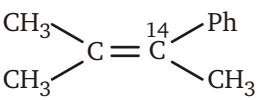
(c) 

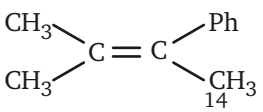
(d) 

61.  Major product of the reaction is:

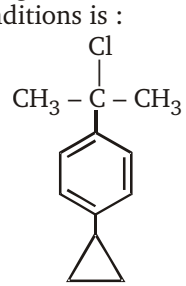
(a) 

(b) 

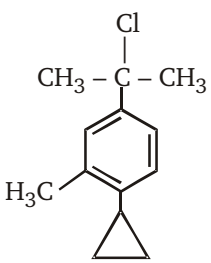
(c) 

(d) 

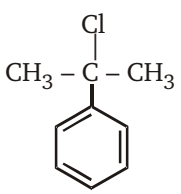
62. The decreasing order of reactivity of the compounds given below towards solvolysis under identical conditions is :



(I)

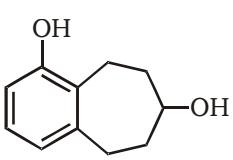


(II)



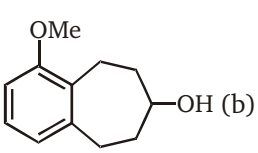
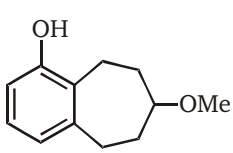
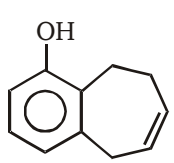
(III)

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

63. 

1. One Eq. NaOH
2. MeBr

(*A*); Product (*A*) is :

(a)  (b)  (c)  (d) None of these

64. (*R*)-2-octyl tosylate is solvolyzed in water under ideal S_{N^1} conditions. The product(s) will be:

(a) *R*-2-octanol and *S*-2-octanol in a 1 : 1 ratio
(b) *R*-2-octanol and *S*-2-octanol in a 1.5 : 1 ratio
(c) *R*-2-octanol only
(d) *S*-2-octanol only

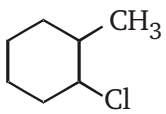
65. From each of the following pairs select the compound that will react faster with sodium iodide in acetone :

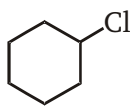
Pair-A: (1) 2 - Chloropropane (2) 2 - Bromopropane

Pair-B: (3) 1 - Bromobutane (4) 2 - Bromobutane

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

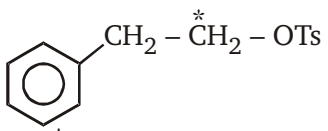
66. Among the given halides, which one will give same product in both S_{N^1} and S_{N^2} reactions.

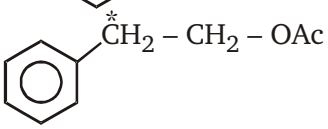
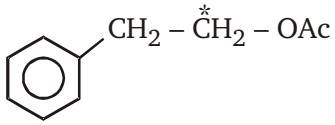
(I) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3$ (II) 

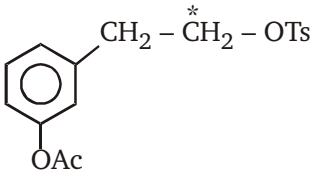
(III)  (IV) $CH_3-\underset{\displaystyle Et}{\underset{|}{CH}}-Br$

(a) (III) only (b) (I) & (II) (c) (III) & (IV) (d) (I), (III) & (IV)

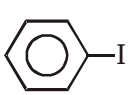
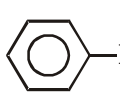
67. Product(s) formed during this reaction is/are :

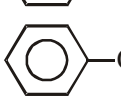
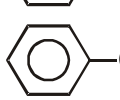
 $\xrightarrow[AcOH]{AcONa}$ Product ? [C^* isotopic carbon]

(a)  (b) 

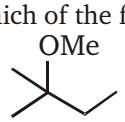
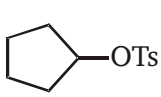
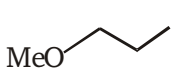
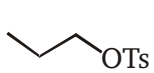
(c)  (d) Both (a) & (b)

68. Anisole $\xrightarrow[\text{reflux}]{\text{excess HI (conc.)}}$ Product

(a)  (b) 

(c)  (d) 

69. Which of the following compounds would react faster with NaCN in an S_{N^2} reaction ?

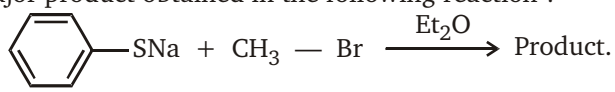
(a)  (b)  (c)  (d) 

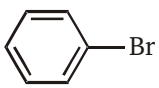
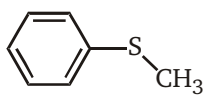
70. HC CNa $Cl-CH_2-CH_2-CH_2-I$ (*A*); Major product (*A*) is :

(a) H – C C – $CH_2-CH_2-CH_2-I$ (b) CH_2 CH – CH_2-I

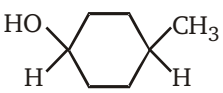
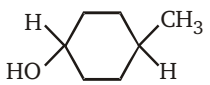
(c) H – C C – $CH_2-CH_2-CH_2-Cl$ (d) CH_2 CH – CH_2-Cl

71. What is the major product obtained in the following reaction ?



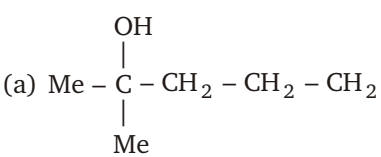
(a)  (b)  (c)  (d) 

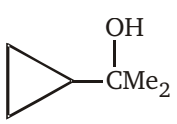
72.  OH S_N2 *A*; The product *A* is :

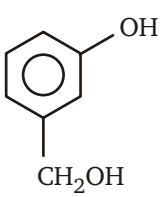
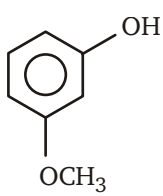
(a)  (b) 

(c) Both (a) and (b) are correct (d) None is correct

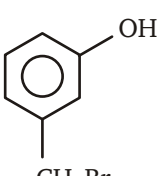
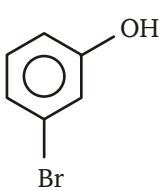
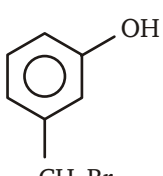
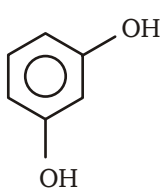
73. Me_2C CH – CH_2-CH_2-Cl $\overset{H_2O}{CaCO_3}$ (*X*); Major product of the reaction is :

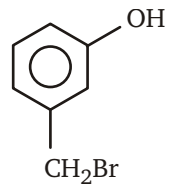
(a)  (b) Me_2C CH – CH_2-CH_2-OH

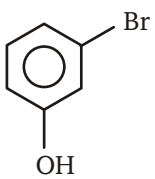
(c) Me_2C CH – CH– CH_2 – OH (d) 

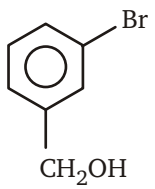
74.  $\overset{HBr}{\longrightarrow}$ (*A*) ,  $\overset{HBr}{\longrightarrow}$ (*B*)

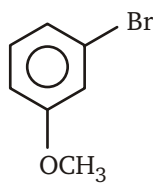
Product (*A*) and (*B*) respectively are :

(a)  and  (b)  and 

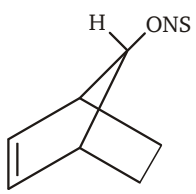
(c) 

and 

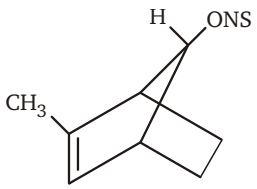
(d) 

and 

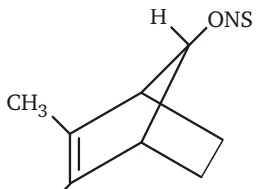
75. Relative rate of reaction with H_2O.



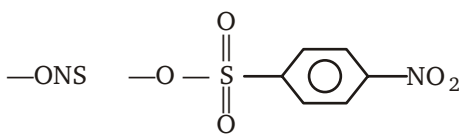
(i)



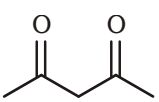
(ii)



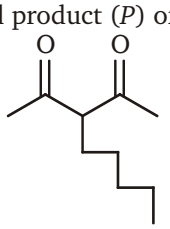
(iii)

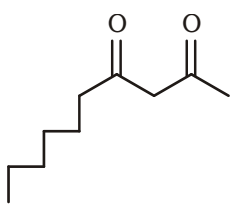


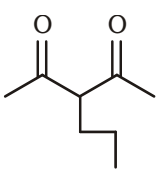
(a) (i) > (ii) > (iii)
(b) (ii) > (i) > (iii)
(c) (iii) > (ii) > (i)
(d) (iii) > (i) > (ii)

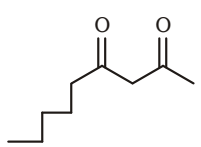
76. 
2 eq. KNH_2
$NH_3(l)$
n—C_4H_9—Br
then H_3O
(*P*) ;

End product (*P*) of the above reaction is :

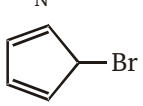
(a) 

(b) 

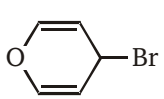
(c) 

(d) 

77. Which of the following statements is correct regarding the rate of hydrolysis of the compounds (*A*) and (*B*) by S_{N^1} reaction ?



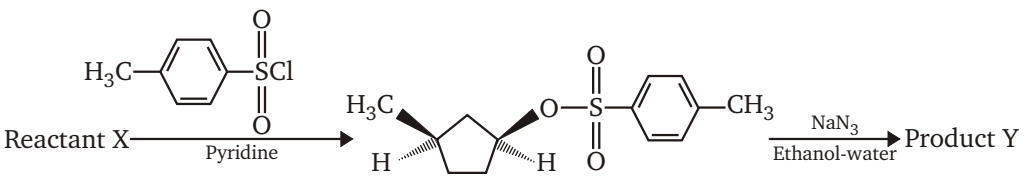
A



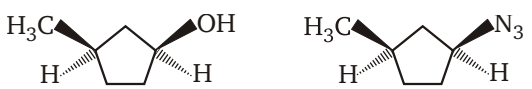
B

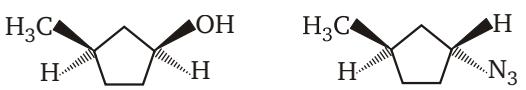
(a) *A* reacts faster than *B*
(b) *B* reacts faster than *A*
(c) Both *A* and *B* reacts at the same rate
(d) Neither *A* nor *B* reacts

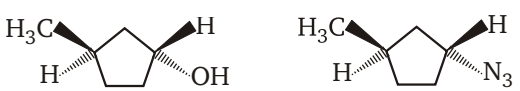
78. What are reactant *X* and product *Y* in the following sequence of reactions ?

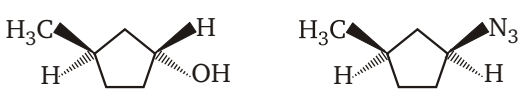


Reactant *X* Product *Y*

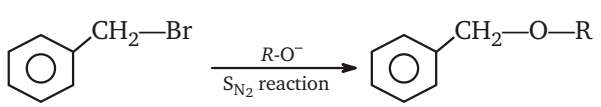
(a) 

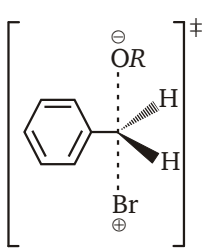
(b) 

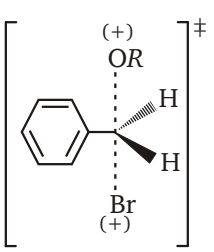
(c) 

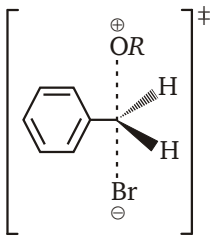
(d) 

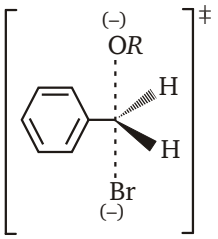
79. Transition state of given S_{N_2} is :



(a) 

(b) 

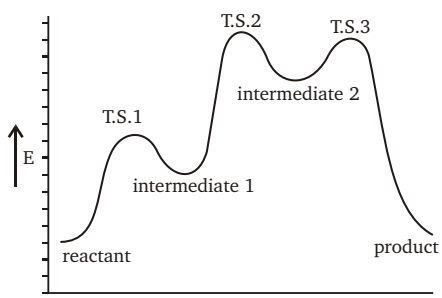
(c) 

(d) 

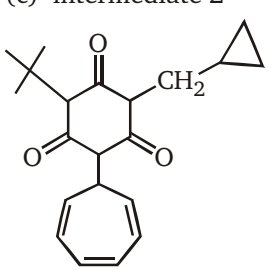
80. $C_6H_{13}Br$ OH $C_6H_{13}OH$ Br is an example of:

(a) Nucleophilic addition
(b) Nucleophilic substitution
(c) Electrophilic addition
(d) Electrophilic substitution
(e) Free radical substitution

81. Transition state 2 is structurally most likely as :



(a) intermediate 1
(b) transition state 3
(c) intermediate 2
(d) product

82. 

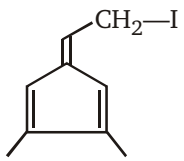
x Number of aromatic compound obtained when above compound undergo complete acidic hydrolysis.

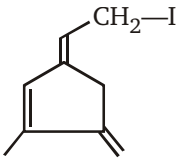
(a) 1 (b) 2 (c) 3 (d) 4

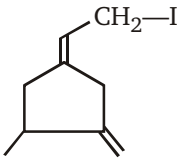
83. S_N1 and S_N2 reactions are

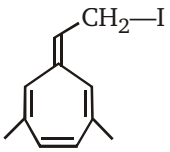
(a) Both stereospecific
(b) Both stereoselective
(c) Stereoselective and stereospecific respectively
(d) Stereospecific and stereoselective respectively

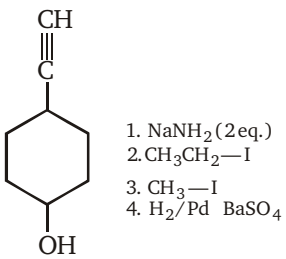
84. Most reactive compound toward S_{N^1} is :

(a) 

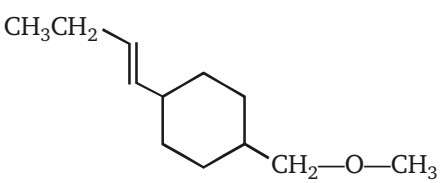
(b) 

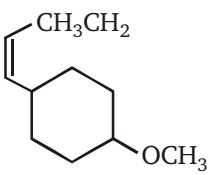
(c) 

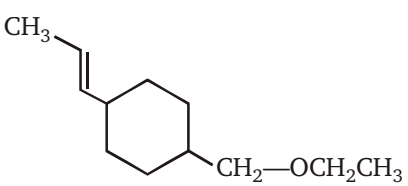
(d) 

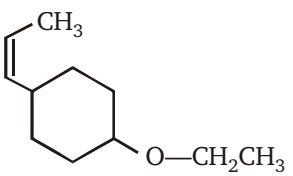
85. 

Product (X) is :

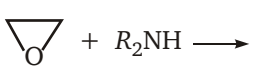
(a) 

(b) 

(c) 

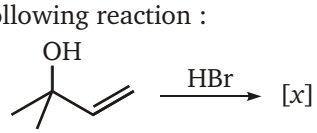
(d) 

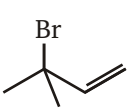
86. Following reaction is an example of :

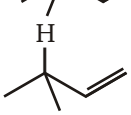


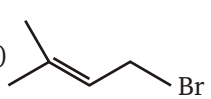
(a) S_N2 Reaction
(b) S_N1 Reaction
(c) Electrophilic Addition
(d) S_N – NGP

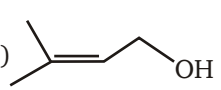
87. The major product of the following reaction :



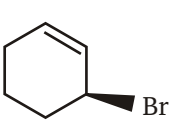
(a) 

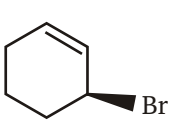
(b) 

(c) 

(d) 

88. Choose the suitable option for the correct mechanism for the following reactions.

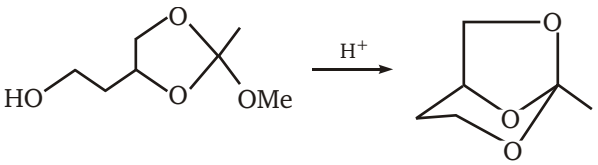
(I) 

+ $CH_3O^{\ominus}$ (high concentration) $\xrightarrow{CH_3OH}$ (II) 

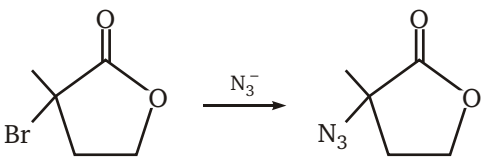
+ CH_3OH ⟶

(a) S_N1, S_N1 (b) S_N1, S_N2 (c) S_N2, S_N1 (d) S_N2, S_N2

89.



Reaction 1

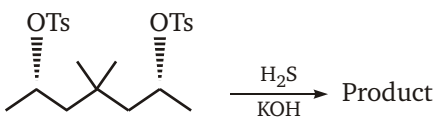


Reaction 2

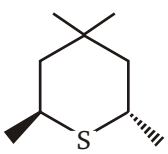
Types of mechanism followed by reaction 1 and reaction 2 respectively.

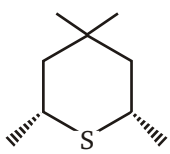
(a) S_N1, S_N1 (b) S_N2, S_N2 (c) S_N1, S_N2 (d) S_N2, S_N1

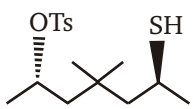
90.

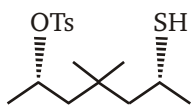


Product of above reaction will be :

(a) 

(b) 

(c) 

(d) 

ANSWERS — LEVEL 1

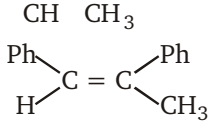
1.	(a)	**2.**	(b)	**3.**	(c)	**4.**	(a)	**5.**	(b)	**6.**	(b)	**7.**	(b)	**8.**	(d)
9.	(b)	**10.**	(a)	**11.**	(c)	**12.**	(a)	**13.**	(d)	**14.**	(d)	**15.**	(b)	**16.**	(c)
17.	(a)	**18.**	(a)	**19.**	(c)	**20.**	(d)	**21.**	(b)	**22.**	(a)	**23.**	(c)	**24.**	(c)
25.	(d)	**26.**	(d)	**27.**	(d)	**28.**	(a)	**29.**	(a)	**30.**	(d)	**31.**	(b)	**32.**	(d)
33.	(d)	**34.**	(c)	**35.**	A(a)	**35.**	B(b)	**36.**	(d)	**37.**	(b)	**38.**	(d)	**39.**	(b)
40.	(d)	**41.**	(d)	**42.**	(a)	**43.**	(c)	**44.**	(b)	**45.**	(c)	**46.**	(d)	**47.**	(a)
48.	(b)	**49.**	(b)	**50.**	(d)	**51.**	(b)	**52.**	(d)	**53.**	(a)	**54.**	(b)	**55.**	(a)
56.	(a)	**57.**	(b)	**58.**	(c)	**59.**	(c)	**60.**	(b)	**61.**	(c)	**62.**	(d)	**63.**	(a)
64.	(b)	**65.**	(c)	**66.**	(d)	**67.**	(d)	**68.**	(c)	**69.**	(d)	**70.**	(c)	**71.**	(c)
72.	(b)	**73.**	(d)	**74.**	(b)	**75.**	(c)	**76.**	(d)	**77.**	(b)	**78.**	(b)	**79.**	(d)
80.	(b)	**81.**	(c)	**82.**	(b)	**83.**	(b,c)	**84.**	(d)	**85.**	(b)	**86.**	(a)	**87.**	(c)
88.	(c)	**89.**	(c)	**90.**	(b)										

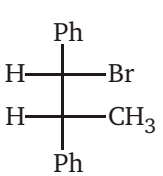
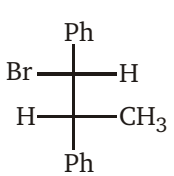
Level - 2

1. **Statement-1 :** Nucleophilicity order in polar-protic solvent is I $<$ Br $<$ Cl $<$ F
Statement-2 : Due to bigger size of I it is less solvated in polar-protic solvent.
(a) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
(b) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
(c) Statement-1 is true, statement-2 is false.
(d) Statement-1 is false, statement-2 is true.

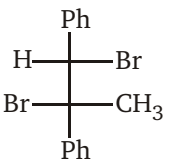
2. **Statement - 1 :** $CH_3\ CH_2\ Cl\ NaI \xrightarrow{\text{Acetone}} CH_3\ CH_2\ I\ NaCl$
Statement- 2 : Acetone is polar-protic solvent and solubility order of sodium halides decreases dramatically in order NaI > NaBr > NaCl. The last being virtually insoluble in this solvent and a 1° and 2° chloro alkane in acetone is completely driven to the side of Iodoalkane by the precipitation reaction.
(a) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for statement-1.
(b) Statement-1 is true, Statement-2 is true and Statement-2 is Not the correct explanation for statement-1.
(c) Statement-1 is true, Statement-2 is false.
(d) Statement-1 is false, Statement-2 is true.

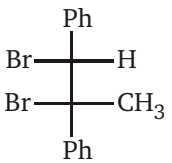
3. Encircle whichever of the following :
(a) is the stronger nucleophile (aprotic solvent) : F or I
(b) is the stronger nucleophile (protic solvent) : F or I
(c) is the stronger base : F or I
(d) is the stronger nucleophile (protic solvent) : NH_3 or NH_2NH_2
(e) is the better leaving group : CH_3COO or CH_3SO_3

4. Encircle whichever of the following :
(a) undergoes an S_{N^2} reaction more rapidly, $CH_3\ Br$ or $CH_3\ \underset{\displaystyle Br}{\underset{|}{CH}}\ CH_3$
(b) undergoes an S_{N^1} reaction more rapidly, $CH_3\ Br$ or $CH_3\ \underset{\displaystyle Br}{\underset{|}{CH}}\ CH_3$
(c) undergoes an E_2 reaction to give (Z)-1,2-diphenylpropene : 

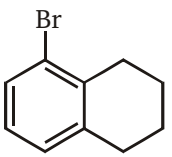

or


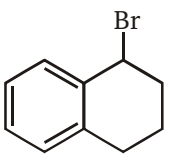
(d) reacts with NaI to give (Z)-1,2-diphenylpropene :



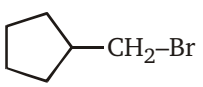
or


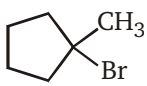
(e) undergoes an S_{N^1} reaction more rapidly,

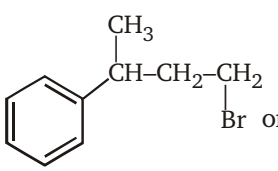


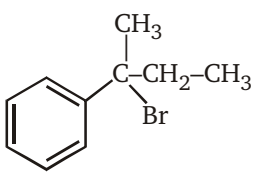
or


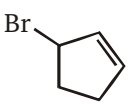
5. Encircle whichever of the following :

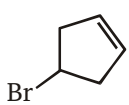
(a) undergoes an S_{N^2} reaction more rapidly : 

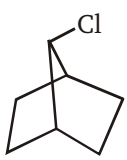
or 

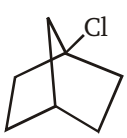
(b) undergoes an E_1 reaction more rapidly : 

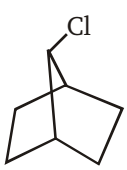
or 

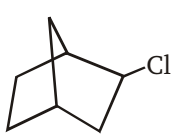
(c) undergoes an S_{N^1} reaction more rapidly: 

or 

(d) undergoes an S_{N^2} reaction more rapidly: 

or 

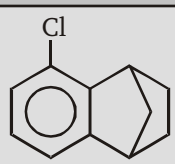
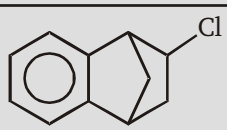
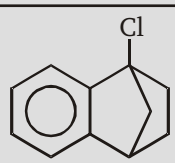
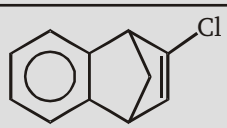
(e) undergoes an E_2 reaction more rapidly : 

or 

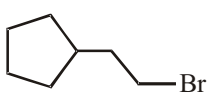
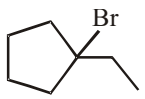
6. Match the column :

Alkyl halide			Relative rate (S_{N^1})		Relative rate (S_{N^2})
(a)	$CH_3 - Br$	**(p)**	1	**(w)**	1200
(b)	$CH_3\ CH_2 - Br$	**(q)**	1.05	**(x)**	40
(c)	$CH_3\ CH(CH_3)\ Br$	**(r)**	11	**(y)**	16
(d)	$CH_3\ C(CH_3)_2\ Br$	**(s)**	1,200000	**(z)**	1

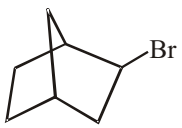
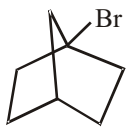
7. Matrix :

Column (I)		Column (II)	
Compound		**Type of reaction**	
(a)		**(p)**	S_{N^1} reaction can take place
(b)		**(q)**	S_{N^2} reaction can take place
(c)		**(r)**	S_{N^1} is not possible
(d)		**(s)**	S_{N^2} is not possible

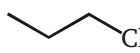
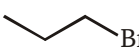
8. Encircle whichever of the following :

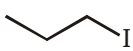
(a) undergoes an S_{N^2} reaction more rapidly,  or 

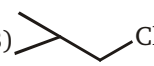
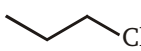
(b) undergoes an S_{N^1} reaction more rapidly, $(CH_3)_3C$ Br or $(CH_3)_3C$ I

(c) undergoes an S_{N^1} reaction more rapidly,  or 

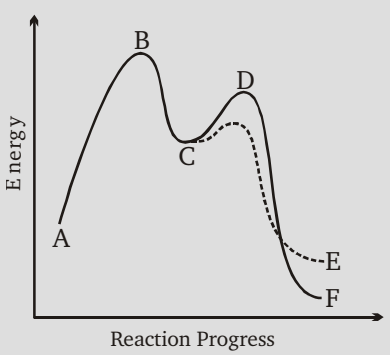
9. Reactivity : Circle the reaction that reacts FASTER by S_{N^2} in each pair :

(1)  $NaOCH_3$  $NaOCH_3$

(2)  OH  NaOH

(3)  NaOH  NaOH

10. Consider the potential energy diagram given below



(X) Name the positions A-D

(Y) Answer the following questions .

(i) Both reaction pathways are : EXOTHERMIC or ENDOTHERMIC

(ii) Which step is the rate determining step (RDS) ? B or D

(iii) Which product is most stable ? E or F

(iv) In accordance with Hammonds postulate, exothermic reactions tend to have

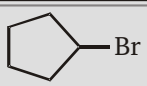
(a) early transition states that are reactant - like

(b) late transition states that are reactant-like

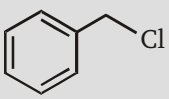
(c) early transition states that are product-like

(d) late transition states that are product-like.

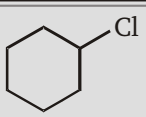
11. Select whether the following combinations of reactants will react by substitution (S_{N^1} or S_{N^2} mechanism), elimination (E_1 or E_2 mechanism)

A.  NaI in acetone, 25 C

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

B.  $NaOCH_3$ in methanol, 50 C

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

C.  $NaOCH_3$ in methanol, 25 C

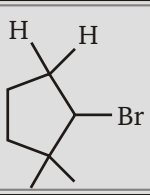
(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

D. $(CH_3)_3C$ OH HBr 48% in H_2O, 25 C

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

E. $(CH_3)_2CH$ Br NaCN in ethanol, 25 C

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

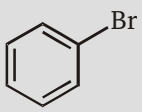
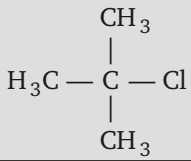
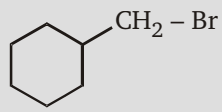
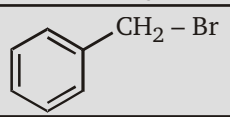
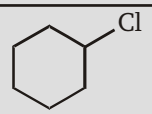
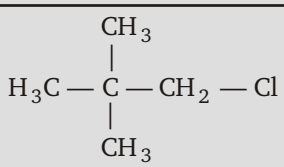
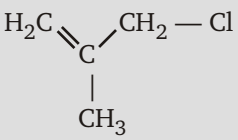
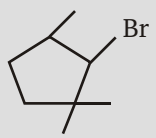
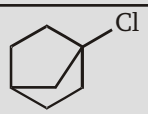
F.  NaCN in ethanol, 25 C

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

G. $(CH_3)_2CHCH_2CH_2$ OH HBr 48% in H_2O, 50 C

(a) S_{N^1} (b) S_{N^2} (c) E_1 (d) E_2

12. Examine the ten structural formulas shown in fig. & select that satisfy each of the following conditions. Write one or more (a through j) in each answer box.

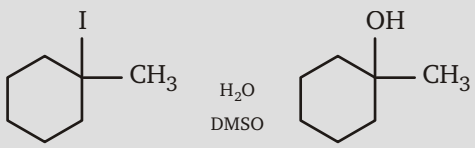
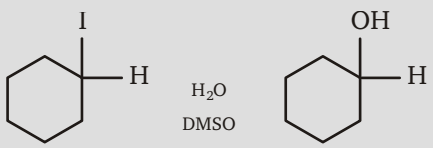
(a)		**(b)**		**(c)**	
(d)		**(e)**		**(f)**	
(g)		**(h)**		**(i)**	
(j)					

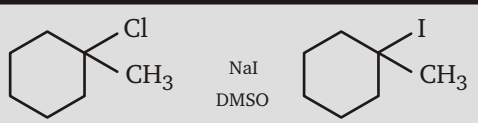
A. Which compounds give an S_{N^2} substitution reaction on treatment with alcoholic NaSH ?

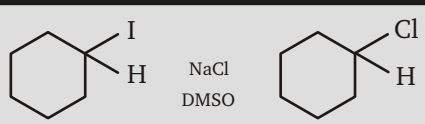
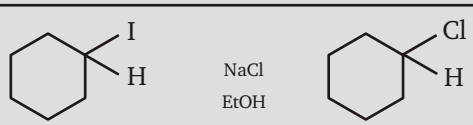
B. Which compounds give an E_2 elimination reaction on treatment with alcoholic KOH ?

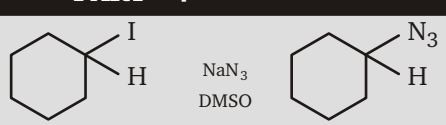
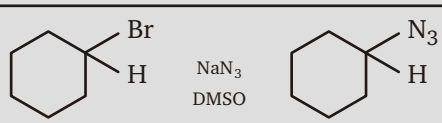
C. Which compounds do not react under either of the previous reaction conditions ?

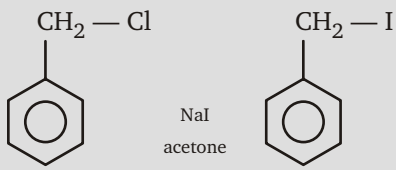
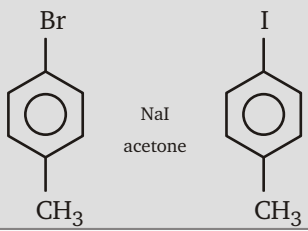
13. Select which reaction from the following reaction pairs will occur faster.

PART - 1	
Reaction A	
Reaction B	

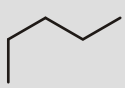
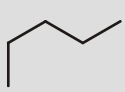
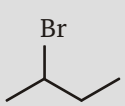
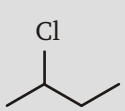
PART - 2	
Reaction C	
Reaction D	

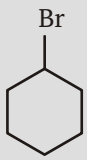
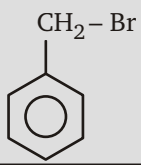
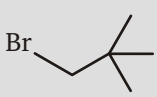
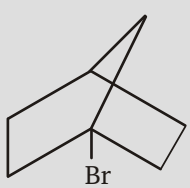
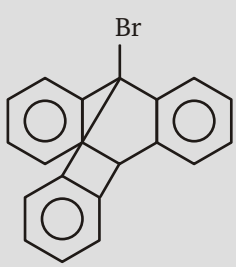
PART - 3	
Reaction E	
Reaction F	

PART - 4	
Reaction G	
Reaction H	

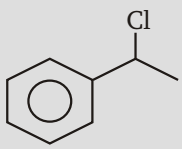
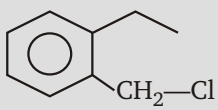
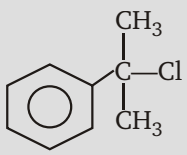
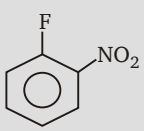
PART - 5	
Reaction I	
Reaction J	

14. Tick your answer in the given box.

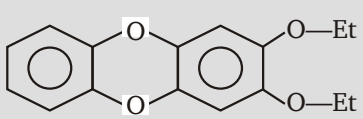
	Alkyl Halide	2-D Structure	Expect S_{N^2} (at a reasonable rate)	
(a)	1-Bromobutane			Yes
				No
(b)	1- Chlorobutane			Yes
				No
(c)	2-Bromobutane			Yes
				No
(d)	2-Chlorobutane			Yes
				No
(e)	2-Chloro-2-methyl propane			Yes
				No

(f)	Bromocyclohexane			Yes
				No
(g)	Bromobenzene			Yes
				No
(h)	Benzyl bromide			Yes
				No
(i)	1-Bromo-2,2-dimethyl propane			Yes
				No
(j)	Bicyclo compound			Yes
				No
(k)	1-bromotriptycene			Yes
				No

15. Match the column

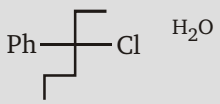
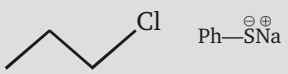
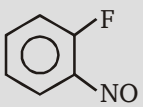
Column-I		Column-II	
(a)		**(p)**	It will undergo Nucleophilic Substitution reaction
(b)		**(q)**	It will undergo E_2 reaction
(c)		**(r)**	It will undergo E_1 reaction
(d)		**(s)**	It will undergo S_{N^2} reaction
		(t)	It will undergo S_{N^1} reaction

16.

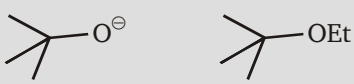
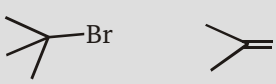
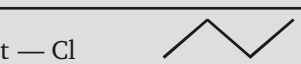


How many (x) moles of HI consumed?

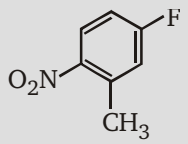
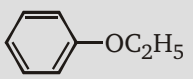
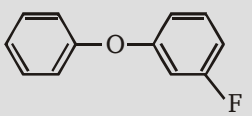
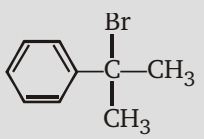
17.

Column (I)		Column (II)	
(a)		**(p)**	S_{N^1}
(b)		**(q)**	S_{N^2}
(c)		**(r)**	Carbocation is intermediate
(d)		**(s)**	Carbanion is intermediate

18.

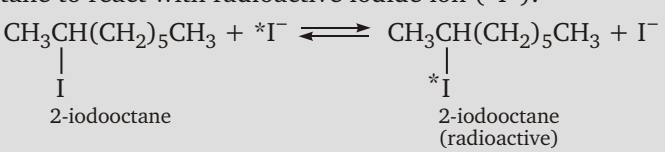
Column (I)		Column (II)	
	(Reaction sequence)		**(Reagent required)**
(a)		**(p)**	$EtO^{\ominus}$
(b)		**(q)**	EtBr
(c)		**(r)**	$EtOH/H^{\oplus}$
(d)		**(s)**	Et–Cl/Na ether

19. Choose the one compound within each set that meets the indicated criterion :

	Column (I)		Column (II)
(a)	The compound that reacts with alcoholic KOH to liberate Halide ion through substitution reaction.	**(p)**	
(b)	The compound that cannot be prepared by a Williamson ether synthesis.	**(q)**	
(c)	The compound that gives an acidic solution when allowed to stand in aqueous ethanol.	**(r)**	
(d)	The ether that cleaves more rapidly in HI.	**(s)**	

20. Comprehension

The first demonstration of the stereochemistry of the S_N2 reaction was carried out in 1935 by Prof. E.D. Hughes and his colleagues at the University of London. They allowed (R)-2-iodooctane to react with radioactive iodide ion (*I–).



The rate of substitution (rate constant K_s) was determined by measuring the rate of incorporation of radioactivity into the alkyl halide. The rate of loss of optical activity from the alkyl halide (rate constant K_o) was also determined under the same conditions.

What ratio K_o / K_s is predicted for each of the following stereochemical scenarios :

A. For inversion reaction :

(a) $\frac{K_o}{K_s}$ 1 (b) $\frac{K_o}{K_s}$ 1 (c) $\frac{K_o}{K_s}$ 1 (d) can not be predicted

B. For equal amounts of both retention and inversion ?

(a) $\frac{K_o}{K_s}$ 1 (b) $\frac{K_o}{K_s}$ 1 (c) $\frac{K_o}{K_s}$ 1 (d) can not be predicted

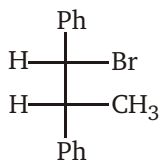
ANSWERS — LEVEL 2

1. d

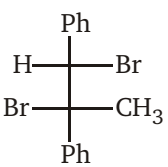
2. c The reaction is Finkelstein reaction.

3. (a) F^-; (b) I^- ; (c) F^-; (d) $NH_2—NH_2$; (e) $CH_3SO_3^-$

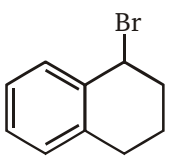
4. (a) CH_3 Br (b) CH_3 CH(Br) CH_3 (c)



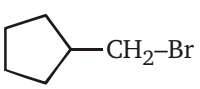
(d)



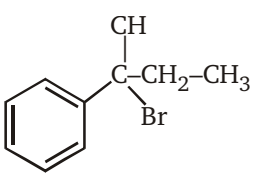
(e)



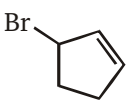
5. (a)



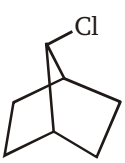
(b)



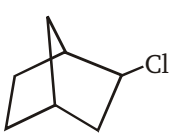
(c)



(d)



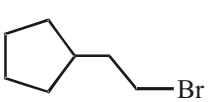
(e)



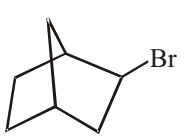
6. a – p, w; b – q, x ; c – r, y; d – s, z

7. a – r, s; b – p, q; c – r, s; d – r, s

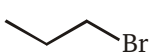
8. (a)



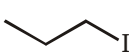
(b) $(CH_3)_3C$ I (c)



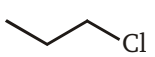
9. (1)



(2)



(3)



10. (X) A- reactants, B-transition state, C-Inter mediate, D- transition state

(Y) (i) exothermic (ii) B (iii) F (iv) a

11. A – b; B – b; C – d; D – a; E – b; F – b; G – b

12. A – c, d, e, f, h; B – b, c, f, i ; C – a, g, j

13.

Part –	1	2	3	4	5
Reaction–	A	D	E	G	I

14.

Yes –	a,	b,	c,	d,	f,	h,
No –	e,	g,	i,	j,	k	

15. a–p, q, r, s, t; b–p,s,t; c–p, q, r t; d–p

16. 2

17. a – p, r; b – q; c – s; d – r

18. a – q; b – p; c – r; d – q

19. a – p; b – r; c – s; d – s

20. A – c; B – a