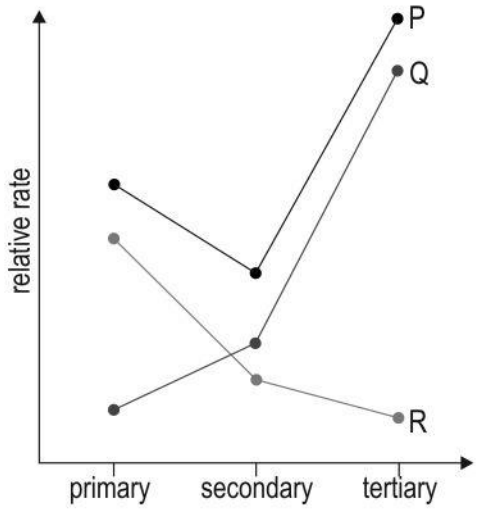
HALOALKANES AND HALOARENES

<table>
<tr><th>Q.No</th><th>Question</th><th>Marks</th></tr>
<tr><td colspan="3">Multiple Choice Question</td></tr>
<tr><td>Q.115</td><td>Three graphs P, Q and R have been drawn to represent the relative rates of hydrolysis reactions for primary, secondary, and tertiary haloalkanes.
 

Which of the following correctly identifies the graphs that represent SN1 and SN2 reactions?
<table><tr><th>Option</th><th>SN_1 reaction</th><th>SN_2 reaction</th></tr><tr><td>W</td><td>graph P</td><td>graph Q</td></tr><tr><td>X</td><td>graph Q</td><td>graph P</td></tr><tr><td>Y</td><td>graph R</td><td>graph Q</td></tr><tr><td>Z</td><td>graph Q</td><td>graph R</td></tr></table>A. W
B. X
C. Y
D. Z</td><td>1</td></tr>
<tr><td>Q.116</td><td>Given below are four haloalkane compounds.

tert-bromobutane, tert-iodobutane, iodobutane, bromobutane

Which of them would be the most easily undergo S_N1 and S_N2 reactions?</td><td>1</td></tr>
</table>

Option	SN_1 reaction	SN_2 reaction
P	tert-iodobutane	iodobutane
Q	tert-bromobutane	bromobutane
R	iodobutane	tert-iodobutane
S	bromobutane	tert-bromobutane

A. P
B. Q
C. R
D. S

Q.117 The table below shows some of the features of S_N1 and S_N2 reaction mechanisms. 1

Rows	S_N1	S_N2
A	first order kinetics	2nd order kinetics
B	reaction favoured by any type of nucleophile	reaction favoured by a non-bulky nucleophile
C	reaction favoured by a good leaving group	reaction not favoured by a good leaving group
D	stereochemistry: racemization	stereochemistry: inversion

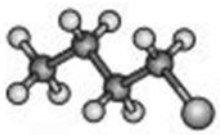
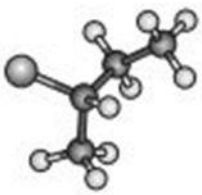
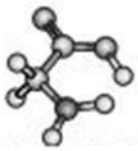
Which of the rows shows an INCORRECT feature for at least one of the mechanisms?

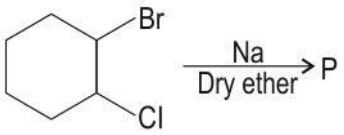
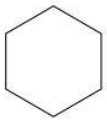
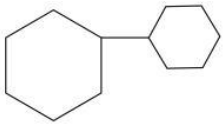
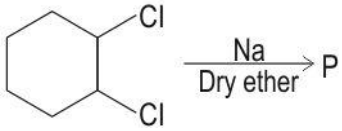
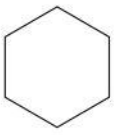
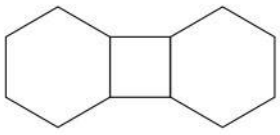
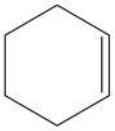
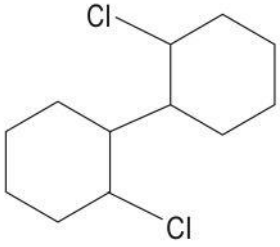
A. A
B. B
C. C
D. D

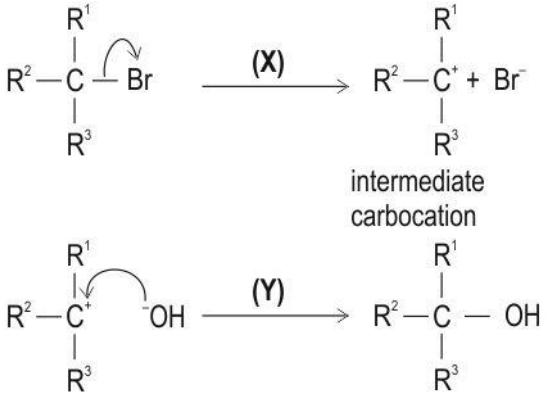
Q.118 Which of the following will be the major product formed in the reaction below? 1

$CH_3 - CH_2 - CH = CH_2 + HBr$ ----> ?

A. $CH_3 - CH_2 - CH_2 - CH_2Br$
B. $CH_3 - CH_2 - CHBr - CH_3$
C. $CH_3 - CHBr - CH = CH_2$
D. $CH_3 - CH = CH - CH_2Br$

Q.119	Which of the following molecules exhibits optical isomerism? A. 3-iodopentane B. 2-iodo-2-methylpropane C. 1,3-diiodopropane D. 2-iodobutane	1
Q.120	The image below shows the ball and stick model of 4 different compounds. A  1 –chlorobutane C  2 –chlorobutane B  2 –aminoethanoic acid D  2, 2 –dimethylpropane How many of the above compounds is/are optically active? A. 1 B. 2 C. 3 D. 4	1
Q.121	Which of the following compounds will be hydrolysed most rapidly under similar reaction conditions? A. 1-chloropropane B. 1-chlorobutane C. 2-chloro-2-methylpropane D. 2-chlorobutane	1
	As per the Fittig reaction, when 2 moles of chlorobenzene reacts with metals such as sodium in the presence of dry ether, it gives diphenyl.	
Q.122	Observe the given reaction.	1

	 Which of the following products will be formed as P? (1)  (2)  (3)  (4)  A. 1 B. 2 C. 3 D. 4	
Q.123	Observe the given reaction.  Which of the following products will be formed as P? (1)  (2)  (3)  (4)  A. 1 B. 2 C. 3 D. 4	1
	Free Response Questions/Subjective Questions	
Q.124	The image below shows different stages for a S_N1 reaction.	2



Which out of the two stages, X and Y, will be slower and why?

Q.125 (i) Consider the reaction between bromopropane and I^- ions. 4

$CH_3CH_2CH_2Br + I^- \text{----> } CH_3CH_2CH_2I + Br^-$

The reaction is carried out in a propanone solvent. The rate law for this reaction is found to be Rate = $k[CH_3CH_2CH_2Br]^x [I^-]^y$ Which mechanism does this reaction follow, S_N1 or S_N2? Justify your answer.

(ii) What will be the rate equation for the reaction $(CH_3)_3CBr$ with I^- ? Justify.

Q.126 The table below gives data about four different gaseous compounds. 3

	Chemical Formula	Atmospheric lifetime (approx. years)	Boiling point (°C)
P	CCl_3F	45	24
Q	CCl_2F_2	114	-29.8
R	$CClF_2CClF_2$	300	3.5
S	CF_4	50,000	-46

(The atmospheric lifetime of a compound is an estimate of the average time it takes for that compound to leave the atmosphere.)

(i) State one problem caused by compound Q in the atmosphere.

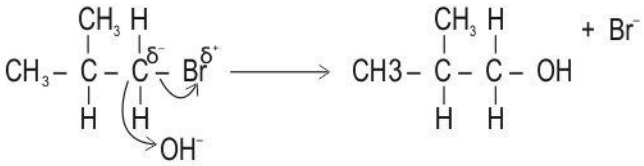
(ii) Which two out of the four compounds are more suitable to be used as a refrigerant in refrigerators and why?

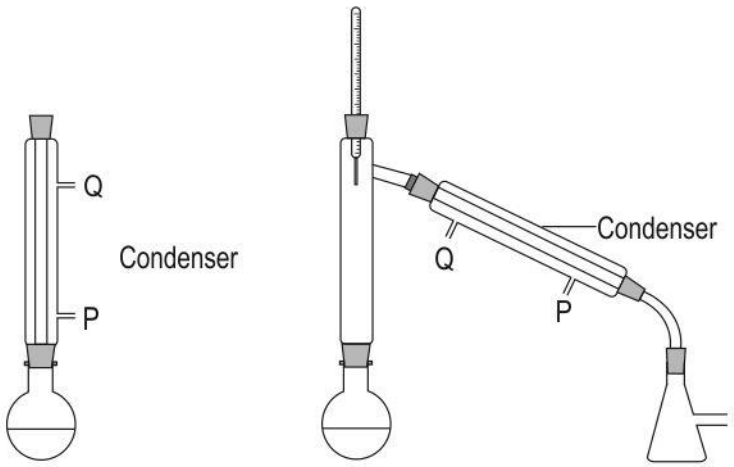
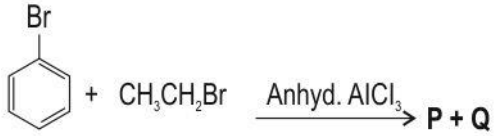
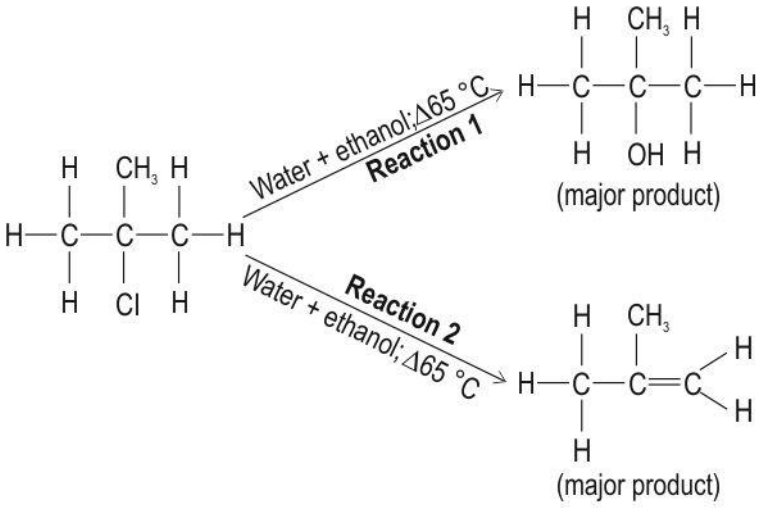
Q.127 For each of the following combinations of reagents and conditions, suggest whether substitution or elimination will predominate. Justify your answer. 3

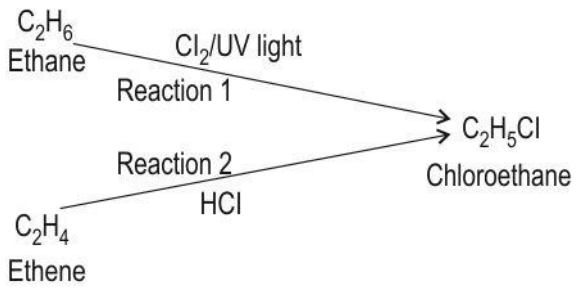
(p) heating $CH_3CH_2CH_2Br$ with aqueous NaOH

(q) heating $(CH_3)_3CBr$ with NaOH in ethanol

(r) heating $(CH_3)_2CHBr$ with $(CH_3)_3CO^-K^+$

Q.128	Show the reaction mechanism for the reaction of tertiary butylbromide with ammonia.	2
Q.129	But-1-ene undergoes electrophilic addition reaction in the presence of HBr. (i) Write the name of all the products formed in the reaction. (ii) Which will be the major product formed and why?	4
Q.130	When 1-bromo-2methylpropane is heated with aqueous alkali, it gives 2-methylpropan-1-ol. Nanda suggested the following mechanism for this reaction.  Identify three mistakes in the mechanism shown by Nanda.	3
Q.131	Do any of the possible structures of $C_5H_{11}Cl$ show stereoisomerism? If no, then explain why. If yes, draw the 3D diagram of the enantiomers.	2
Q.132	1-bromobutane is prepared from 1-butanol as per the reaction below. $C_4H_9OH + NaBr + H_2SO_4$ ---> $C_4H_9Br + NaHSO_4 + H_2O$ Given below are the different stages in the preparation. (1) heating the reactants for around 50 minutes in the apparatus shown in figure 1 (2) distilling the reaction mixture to obtain the product 1-bromobutane in the apparatus shown in figure 2 (3) weighing the distillate obtained (a) Explain why the reactants are heated for 50 minutes in stage 1. (b) What is the function of condensor in stage 1 and in stage 2? How does it help the reaction?	3

	 Figure 1 P - water in Q - water out Figure 2	
Q.133	In the reaction below,  (i) Identify P and Q. (ii) Which of them is the major product and why?	3
Q.134	The image below shows two competing routes or reactions when a haloalkane reacts with water in the presence of alcohol. The major products under each of the routes are shown.  (i) Explain the mechanism for both these reactions. (ii) Which out of two reactions will predominate? Give reasons.	4
Q.135	Haloalkanes are important compound which are produced at scale for industrial purpose. To increase the efficiency and reduce the cost of production, scientists use different combinations of reactants and reaction conditions.	2

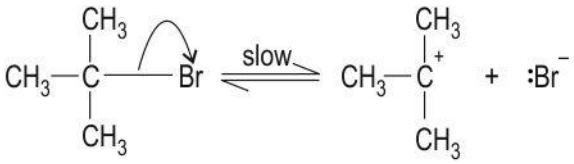
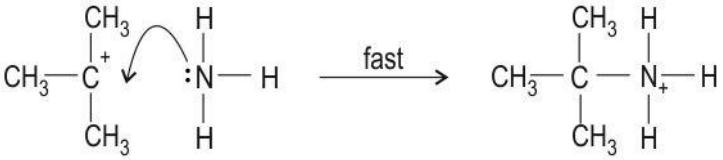
<table>
<tr><td></td><td>You are given two different compounds that can be used to make C_2H_5Cl as shown below.
 

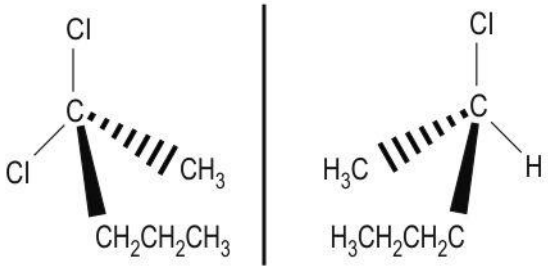
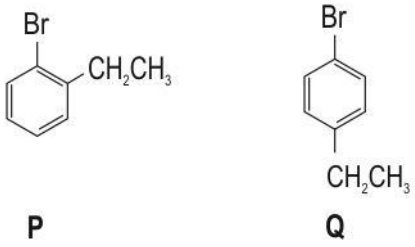
Which out of two reactants will you choose and why?</td><td></td></tr>
<tr><td>Q.136</td><td>Study the reaction below and answer the questions that follow:
$CH_3Cl + NaI \rightarrow CH_3I + NaCl$
(i) How can we increase the rate of the forward reaction?
(ii) If methyl fluoride is to be prepared by the above process, state the reactants?
(iii) Arrange methyl iodide, methyl fluoride and methyl chloride in the decreasing order of their dipole moment.</td><td>3</td></tr>
<tr><td>Q.137</td><td>An organic compound with the formula C_6H_5Br reacts with CuCN to form compound ‘P’ and CuBr in presence of pyridine at 475 K. Compound P on reaction with dil. HCl forms compound ‘Q’ which reacts with methyl alcohol produces a sweet smelling compound ‘R’.
Write the chemical reaction showing the above conversions.</td><td>3</td></tr>
<tr><td>Q.138</td><td>Give a reason why vinyl halides generally do not undergo nucleophilic substitution reactions.</td><td>1</td></tr>
<tr><td>Q.139</td><td>To prepare a Grignard reagent, Udita mixes magnesium metal in dry ether with the compound shown below.
CH_3 - CHOH - CH_2 - CH_2Br
Will she obtain the Grignard reagent? Justify your answer.</td><td>1</td></tr>
<tr><td>Q.140</td><td>The table below shows the effect of aqueous silver nitrate on bromine containing compounds at room temperature.
<table><tr><th>Sodium bromide</th><th>1 - bromobutane</th></tr><tr><td>pale yellow precipitate appears immediately</td><td>no reaction at first;faint precipitate appears after several minutes</td></tr></table></td><td>3</td></tr>
</table>

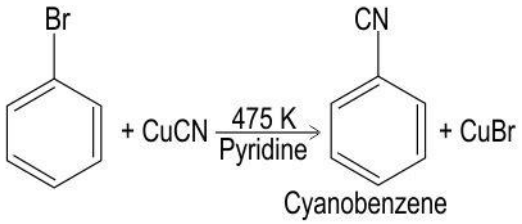
	(i) Why does silver nitrate produce no immediate precipitate with 1-bromobutane? (ii) Suggest a reason why a precipitate appears after several minutes.	

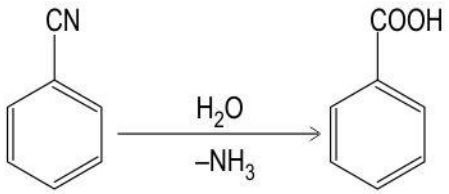
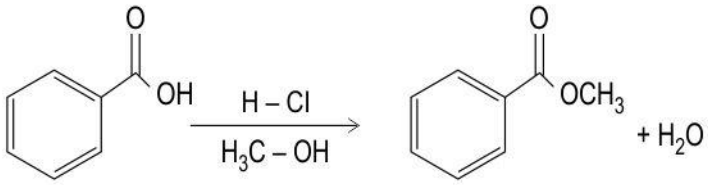
Answer Key and Marking Scheme

Q.No	Answers	Marks
Q.115	D. Z	1
Q.116	A. P	1
Q.117	C. C	1
Q.118	B. CH_3 - CH_2 - CHBr - CH_3	1
Q.119	D. 2-iodobutane	1
Q.120	A. 1	1
Q.121	C. 2-chloro-2-methylpropane	1
Q.122	C. 3	1
Q.123	C. 3	1
Q.124	(i) X will be slower [1] - X involves breaking of C-Br bond to form a carbocation [0.5] - the carbocation is very unstable and reactive so the second step will be fast [0.5]	2
Q.125	(i) S_N2 [1] - because in S_N2 reaction the incoming nucleophile (I^-) interacts with the substrate (bromopropane) causing the C - Br bond to break and a new C - I bond to form. These two processes occur simultaneously in a single step without the formation of any intermediate. The rate of reaction is determined by the concentrations of both the reactants. [1] (ii) Rate = k[$(CH_3)_3CBr$] given by S_N1 [1] - because S_N1 is a two step mechanism in which there is an intermediate carbon cation formed. The rate of reaction is determined only by the concentration of bromopropane. [1]	4
Q.126	(i) CCl_2F_2 decomposes under UV light to give free radical chlorine which reacts with ozone and destroys the ozone layer. (ii) Compounds Q and S; [1]	3

	- It is very important that the refrigerant has a low boiling point, so that it turns into gas easily when it absorbs heat. [1]	
Q.127	(p) Substitution; In polar solvent, substitution predominates for primary haloalkanes with OH ions [1] (b) Elimination; In a less polar solvent like alcohol, elimination predominates for tertiary haloalkanes with OH ions [1] (c) Elimination; elimination predominates due to steric effect as the base used is bulky group [1]	3
Q.128	The mechanism involves an initial ionisation of the halogenoalkane to form a carbocation:  [1] - This is followed by a very rapid attack by ammonia on the carbocation formed:  [1]	2
Q.129	(i) 2-bromobutane and 1-bromobutane (ii)2-bromobutane [1] - During the reaction, intermediate primary and secondary carbocations are formed. [0.5] - Secondary carbocations are energetically more stable than primary carbocations due to positive inductive effect. [1] - The secondary carbocation will be formed in preference to the primary carbocation – hence, the major product will be 2-bromobutane not 1-bromobutane. [0.5] (give marks if they explain using equations instead of text to explain)	4
Q.130	1 mark each for the following: - C-Br dipole is reversed - OH^- to C arrow is reversed	3

	- lone pair of electrons is missing from OH^-	
Q.131	- Yes; structure of enantiomers:  	2
Q.132	(a) This substitution reaction is very slow in nature and hence takes a long time. (accept any other valid answer) (b) 1 mark each for the following: - In stage 1, it condenses vapours and returns liquid to the flask thus allowing the reaction mixture to be heated at the boiling point without any loss of the reactant. - In stage 2, it condenses vapours of the product that is distilling out.	3
Q.133	(i)  **P** **Q** (ii) Q is the major product [1] - Due to the steric effect of the bromine group, substitution at the ortho position is hindered and preferably occurs at the para position. (give marks if they mention less repulsion instead of steric)	3
Q.134	(i) - For reaction 1, water can behave as a nucleophile and donate a lone pair (from oxygen) and attack (positive) carbon (originally attached to Cl) carbocation [1] - For reaction 2, water behave as a base and accepts a hydrogen ion/proton. This leads to elimination of HCl from the reactant. [1]	4

	(ii) Reaction 2 [1] Reasons: - Tertiary carbocation formed during intermediate stage is stabilized by the electron density from three alkyl groups [0.5] - To avoid bulky group effect, elimination reaction dominates over substitution reaction [0.5]	
Q.135	- C_2H_4 - By reaction 2, a single product is obtained. - Whereas by reaction 1, a mixture of mono, di and tri-substituted products are formed. This reduces efficiency and increases cost of production. (Accept any other correct answer)	2
Q.136	(i) The rate of the reaction can be improved by precipitating NaCl in dry acetone. (ii) The reactants needed to prepare methyl fluoride is methyl chloride or methyl bromide and any metallic fluoride such as AgF, Hg_2F_2 , CoF_2 or SbF_3. (iii) The decreasing order of their dipole moment is: methyl fluoride> methyl chloride > methyl iodide. *[Give 1 mark for each correct answer. Marks should be granted if the answer is written correctly in own words.]*	3
Q.137	The chemical reactions showing the conversions are: Formation of P:  **P** Compound 'P' is cyanobenzene. Formation of Q:	3

	 **P** **Q** Compound 'Q' is benzoic acid. Formation of R:  **Q** **R** Compound 'R' is Acetophenone. *[Give 1 mark for each correct conversion]*	
Q.138	Vinyl halides generally do not undergo nuclepohilic substitution reactions. This is because the partial double bond character of the C-Cl bond makes it difficult to break.	1
Q.139	- She will not obtain the Grignard reagent. [0.5] - As the Grignard reagent is formed it will immediately be protonated by the alcoholic group in the compound X. [0.5]	1
Q.140	(i) The C-Br bond in 1-bromobutane is covalent in nature, therefore it does not produce Br ions immediately. (ii) Bromine is more electronegative than carbon, so the C-Br bond is polar [0.5] - The partial positive charge on carbon attracts nucleophiles with their lone pairs of electrons. [0.5] - Water molecules from silver nitrate attack the partial positive carbon, and a substitution reaction takes place, releasing bromine ions after some time. [1]	3