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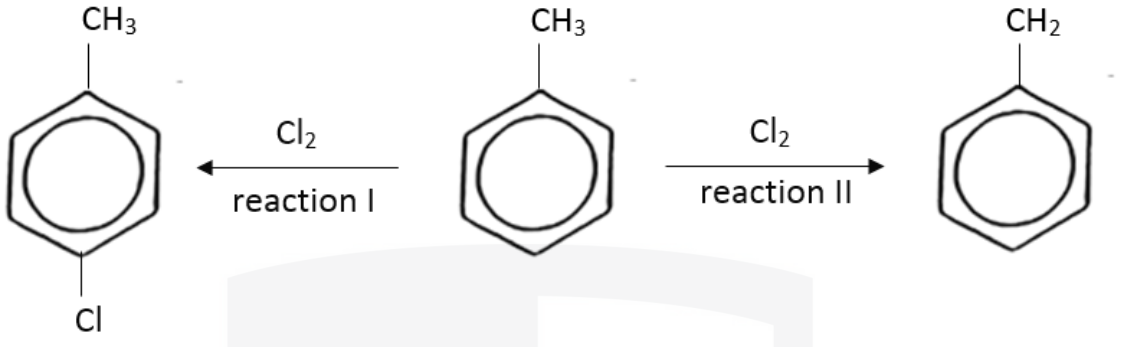
CHEMISTRY
ORGANIC CHEMISTRY

Level & Board	CIE (A-LEVEL)
TOPIC:	Halogen Derivatives
PAPER TYPE:	QUESTION PAPER - 1
TOTAL QUESTIONS	11
TOTAL MARKS	105

Halogen Derivatives - 1

1)

This question is concerned with organochlorine compounds.



A B

(i) conditions for reaction I

(ii) conditions for reaction II

(b) State the reagent needed to carry out the following reaction.

C

reagent for reaction III: **[1]**

(c) The three chloro-compounds A, B and C vary in their ease of hydrolysis.

(i) Place a tick in the box corresponding to the correct relative rates of hydrolysis.

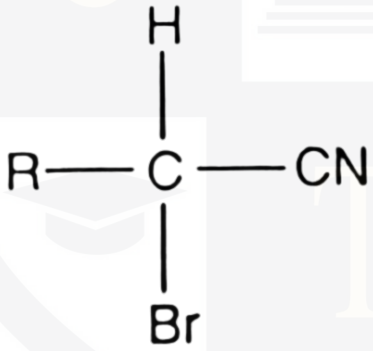
[the symbol '>' means 'faster than']

	Place one tick only in this column
A > B > C	
A > C > B	
B > A > C	
B > C > A	
C > B > A	
C > A > B	

(ii) Suggest an explanation for these differences in reactivity. **[3]**

2)

Compound G, in which R – represents the rest of the molecules, was made for use as a tear gas in World War 2.



compound **G**

Compound G was made by the following sequence of reactions.

$$R-CH_3 \xrightarrow{stage\ I} R-CH_2Cl \xrightarrow{stage\ II} R-CH_2CN \xrightarrow{stage\ III} R-CHBrCN$$

(a) (i) For stage I and for stage II, state the reagent (s) and condition(s) used to carry out each change.

(ii) Suggest the reagent(s) and condition(s) necessary to carry out stage III.

[6]

3)

(b) Describe the mechanism of the reaction between bromoethane and sodium cyanide. **[3]**

(b) Identify the compounds J – M in the following reactions

(i) $(CH_3)_2CHCH_2Br \xrightarrow{hot\ KOH\ in\ ethanol} J$

(ii) $(CH_3)_2\ CHBr \xrightarrow[(in\ ethanol)]{KOH} K \xrightarrow[\substack{followed\ by\ ethanol.\\ conc.\ H_2SO_4 and\ heat}]{heat\ with\ H_2SO_4(aq)}$ L

(iii) $BrCH_2CH_2Br + \underset{(in\ an\ excess)}{CH_3CH_2NH_2} \xrightarrow[(in\ ethanol}]{} M$ [4]

4)

Halogenoalkanes are readily hydrolysed by OH- ions to form alcohols. Primary halogenoalkanes and tertiary halogenoalkanes are hydrolysed by different mechanisms.

(a) Describe the mechanism of the hydrolysis of CH_3CH_2Br. In your answer show any relevant charges, dipoles or one pairs of electrons you consider to be important in this mechanism.

(b) 3-bromopropene, CH_2=$CHCH_2Br$, can be hydrolysed by NaOH(aq) to term CH_2=$CHCH_2OH$. Results of an investigation into the kinetics of this reaction are given below.

experiment number	[CH_2=$CHCH_2Br$] /mol dm^{-3}	[NaOH] /mol dm^{-3}	Relative initial rate
1	9.10	0.20	1.00
2	0.20	0.10	2.00
3	0.30	0.20	3.00
4	0.60	0.40	6.00

(i) Use the data in the table to deduce the order of reaction with respect to CH_2=$CHCH_2Br$ and with respect to NaOH.

order with respect to CH_2=$CHCH_2Br$

order with respect to NaOH

(ii) Write an overall rate equation for the reaction between CH_2 = $CHCH_2Br$ and NaOH. **[3]**

(c) (i) is the mechanism of this hydrolysis the same as or different from the one you have described in (a)? Explain your answer.

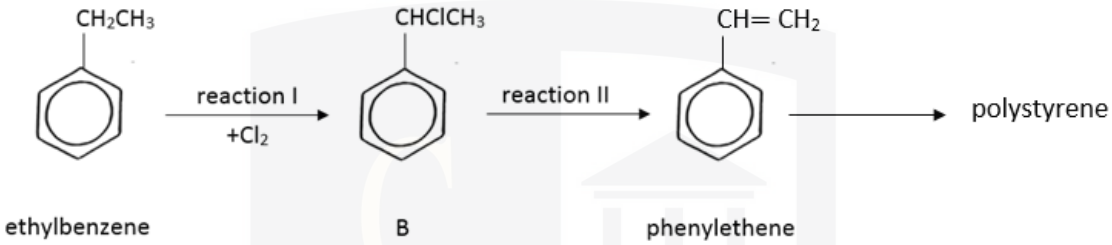
(ii) Suggest the structure of the intermediate formed in the hydrolysis of CH_2 = $CHCH_2Br$.

(d) The bromine atom in $CH_2 = CHCH_2Br$ is very reaction.
The bromine atom in $CH_2 = CHBr$ is unreactive.

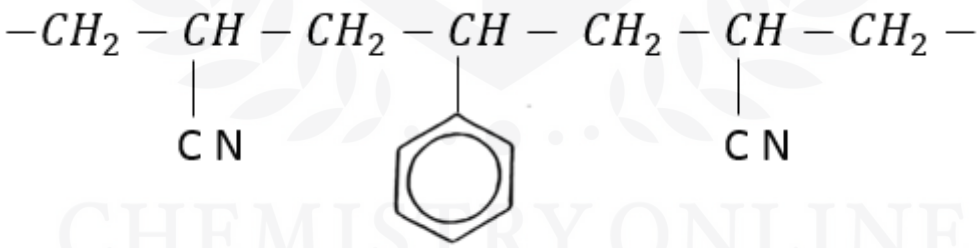
[2]

5)

Ethylbenzene is an important starting material for making polystyrene (poly(phenylethene)).



(a) (i) State the conditions needed to carry out reaction I in the laboratory.
(ii) State the reagent and conditions needed for reaction II.
(iii) Draw the structure of the repeat unit of polystyrene.
(iv) There are several polymers that consist of phenylethene co-polymerised with other monomers. The following formula shows part of the chain of one such co-polymer.



Deduce the structural formula of the other monomer. **[5]**

6)

One method of making 1-bromobutane in the laboratory is described below.

Stage 1	Place 35 g of powdered sodium bromide. 30cm^3 of water. and 25cm^3(20g) of butan-1-ol, in a 250cm^{3}two necked flask fitted with a tap funnel and reflux condenser.
Stage 2	concentrated sulfuric acid (25cm^3) is then placed in the tap funnel and added drop by drop to the reagents in the flask, keeping the contents well shaken and cooled occasionally in an ice-water bath.

(a) The overall reaction may be considered to take place in two stages. In the first stage the inorganic reagents react together to form HBr. In the second stage, the organic reagent reacts with the HBr that is formed in the first stage. Write an equation for each of these stages. **[2]**

(b) In this preparation by using the amounts given above. One of the regents, sodium bromide or buan-1-ol, will be present in an excess.
Use your equations in (a) and the data above to determine, by calculation, which regent is in an excess. **[2]**

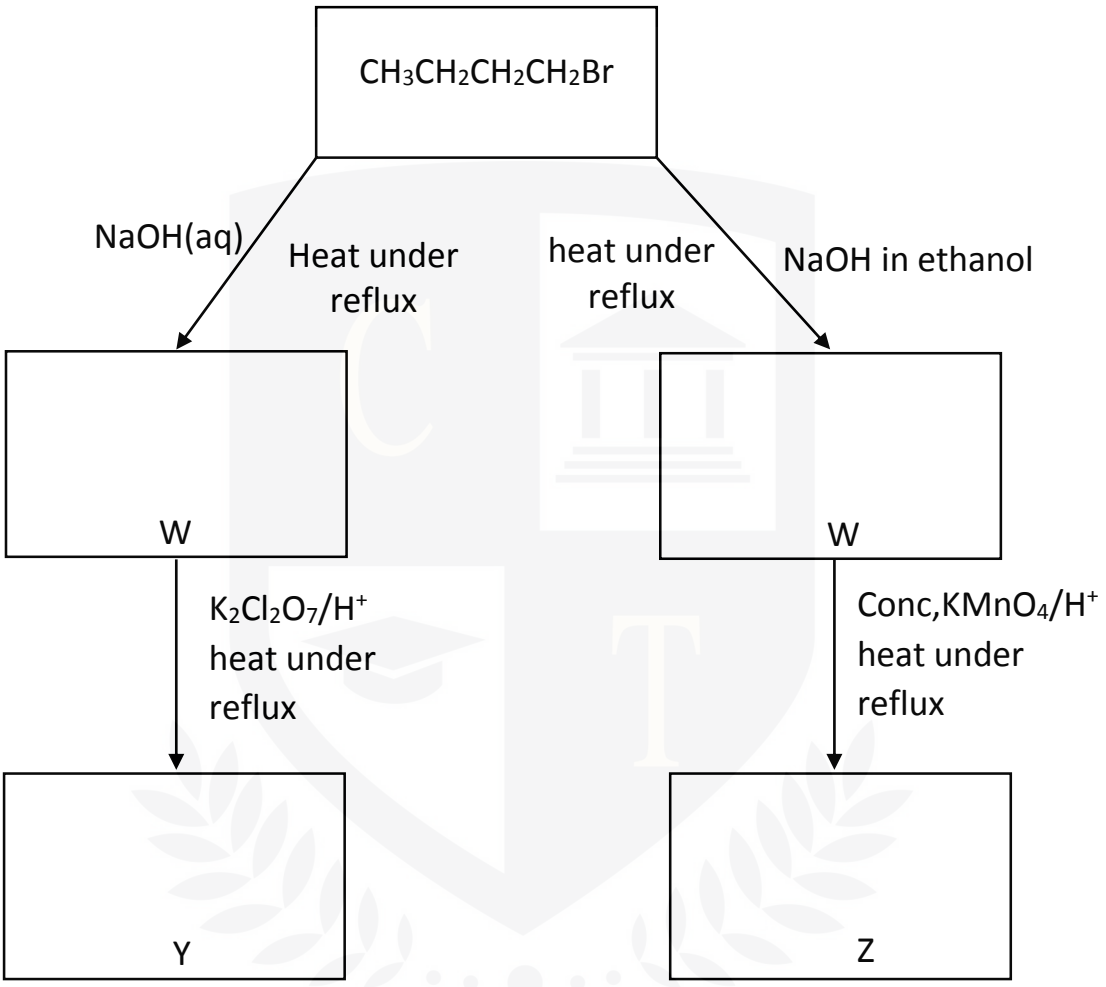
(c) In an laboratory preparation of 1-bromobutane, when 15.4 g of butan-1-ol was used, 22.5 g of 1-bromobutane was obtained after purification.
Calculate the yield of 1-bromobutne as a percentage of the theoretical maximum yield. **[2]**

(d) When the concentrated sulfuric acid is added to the reaction mixture (stage 2), unless the temperature is controlled carefully, the acid may react with either of the original reactants (sodium bromide or butan-1-ol) to give at least two by-products, one of which is inorganic and the other organic. What inorganic and organic by-products may be formed?
In each case, identify one by-product and state the role of the concentrated sulfuric acid in the formation of this by-product.

[4]

7)

(a) Complete the following reaction scheme which starts with 1-bromobutane. In each empty box, write the structural formula of the organic compound that would be formed.



[4]

(b) One of the compounds W,X,Y or Z can be polymerized.

(i) identify this compound by its letter.

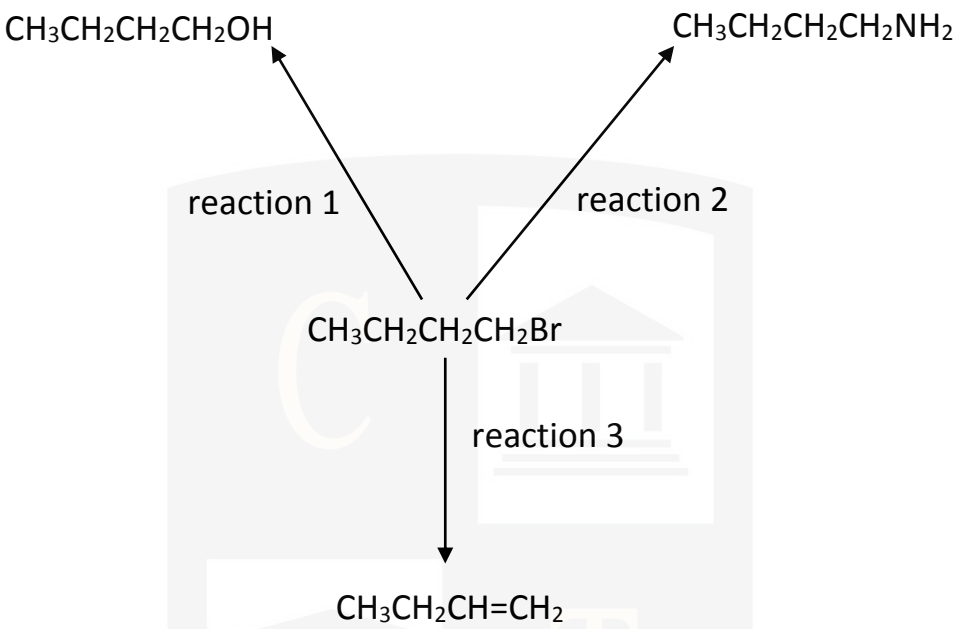
(ii) Draw a section of the polymer chain formed by this compound.

Show two repeat units. **[2]**

8)

Halogenoalkanes have many chemical uses, particularly as intermediates in organic reactions.

Three reactions of 1-bromobutane, $CH_3CH_2CH_2CH_2Br$, are shown below.



(a) For each reaction, state the reagent and solvent used. **[6]**

(b) When 1-iodobutane, $CH_3CH_2CH_2CH_2I$, is reacted under the same conditions as those used in reaction 1, butan-1-ol is formed.
What difference, if any, would there be in the rate of this reaction compared to the ration of 1-brombutane?
Use appropriate data from the *Data Booklet* to explain your answer. **[3]**

Dichlrodifluoromethane, $CCll_2F_2$, is an example of a chlorofluorocarbon (CFC) that was formerly used as an aerosol propellant. In September 2007, at the Montroleal summit, approximately 200 countries agreed to phase cut the use of CFCs by 2020.

(c) State two properties of CFCs that made them suitable as aerosol propellants. **[2]**

(d) When CFCs are present in the upper atmosphere, hemolytic fission takes place in the presence of ultraviolet light.

(i) What is meant by the term *hemolytic* fission?

(ii) Suggest an equation for the hemolytic fission of CCl_2F_2.

[2]

(e) The most common replacements for CFCs as aerosol propellants are hydrocarbons such as propane and butane.

Suggest one disadvantage of these compounds as aerosol propellants.

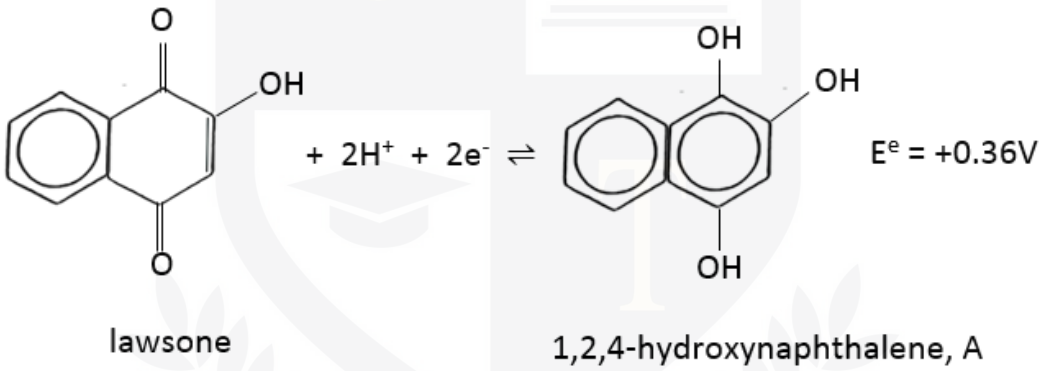
[1]

9)

Lawsone is the dye that is extracted from the henna plant, Lawsonia inermis.

Although its natural color is yellow, lawsone reacts with the proteins in hair and skin to produce the characteristic brown henna color.

Lawsone can readily be reduced to 1,2,4-frihydroxynaphthalene, compound **A**.



(a) (i) Name three functional groups in lawsone.

(ii) Describe a reaction (reagent with conditions) that you could use to distinguish lawsone from compound A.

(iii) Suggest a reagent that could be used to convert lawsone into compound A in the laboratory.

(iv) Draw the structural formula of the compound formed when lawsone is reacted with $Br_2(aq)$. **[6]**

(b) Compound **A** can be oxidized to lawsone by acidified $K_2Cr_2O_7$.

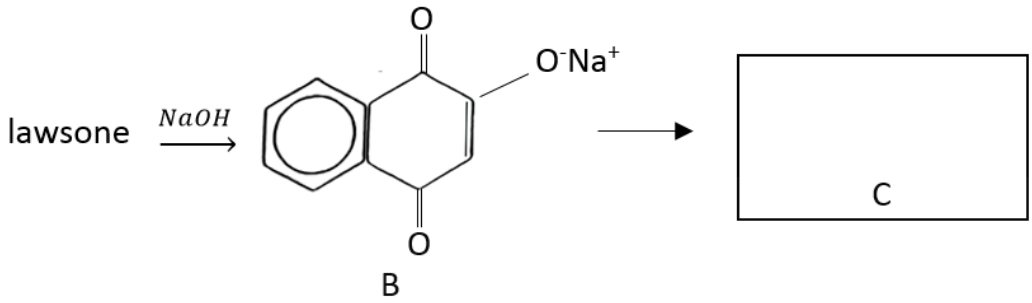
(i) Use the Data Booklet to calculate the $E^{\ominus}_{cell}$ for this reaction.

(ii) Construct an equation for this reaction. Use the molecular formulae of lawsone, C10H6O3, and compound A, $C_{10}H_8O_3$, in your equation.

(iii) When 20.0 cm^3 of a solution of compound A was acidified and titrated with 0.0500 mol dm^{-3} $K_2Cr_2O_7$, 7.50 cm^3 of the $K_2Cr_2O_7$ solution was needed to reach the end-point.

Calculate [A] in the solution. **[5]**

(c) When lawsone is reacted with NaOH(aq), compound B is produced.



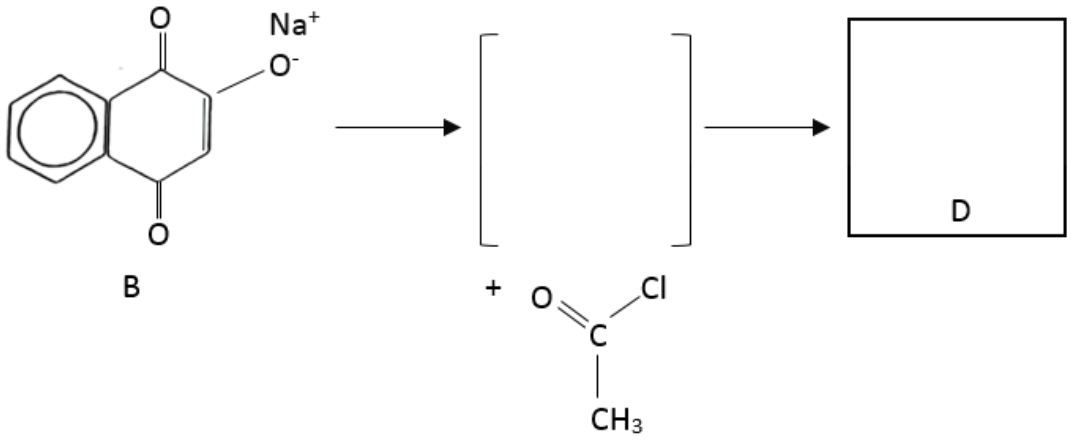
Reacting B with ethanoyl chloride, CH_3COCl, produces compound C, with the molecular formula $C_{12}H_8O_4$.

(i) Suggest the identity of compound **C**, and draw its structure in the box above.

Another compound, **D**, in addition to **C**, is produced in the above reaction. D is an isomer of **C** which contains the same functional groups as **C**, but in different t positions.

(ii) Suggest a possible structure for **D**.

(iii) Suggest a mechanism for the formation of **D** from **B** and ethanoyl chloride by drawing relevant structures and curly arrows in the following scheme.

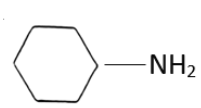
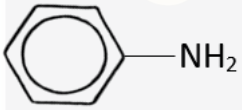


[3]

10)

(a) Describe and explain how the acidities of $CHCl_2CO_2H$ are CH_2ClCO_2H compare to each other, and to the acidity of ethanoic acid. **[3]**

(b) For each of the following pairs of compounds, suggest one chemical test (reagents and conditions) that would distinguish between them. State the observations you would make with each compound, writing 'none' it appropriate.

first compound	Second compound	Test (reagents and conditions)	Observation with first compound	Observation with second compound
				
CH_2CH_2COCl	CH_2COCH_2Cl			
CH_3CH_2CHO	CH_3COCH_3			

[7]

(c) The following diagram shows a section (not a repeat unit) of a polymer, G, that can be made from the two monomers **E** and **F**.

diagram

(i) What *type of polymerization* made this polymer?

(ii) Draw the structures of the two monomers **E** and **F**.

E

F

(iii) Suggest the conditions needed to make polymer **G** from **E** and **F** in the laboratory.

(iv) One of the monomers, **E** or **F**, could be changed to make a more rigid polymer of a similar chemical type to **G**.

Suggest which of your tow monomers could be changed, and suggest a structure for the new monomer. **[6]**

11)

(a) Explain what is mean by the term *bond energy*. **[2]**

(b) (i) Describe and explain the trend in bond energies of the C – X bond in halogenoalkanes, where X = F, Cl, Br or I.

(ii) Describe the relationship between the reactivity of halogenoalkanes, RX, and the bond energies of the C – X bond **[3]**

(c) Use the Data Booklet to suggest an explanation as to why CFCs such as CF_2Cl_2 are much more harmful to the ozone layer than fluorocarbons such as butane, C_4H_{10}.

[3]

(d) Predict the products of the following reactions and draw their structures in the boxes below. The molecular formula of each product is given, where X = Cl, Br or I.

diagram

[3]

(e) Ethane reacts with chlorine according to the following equation.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

(i) State the conditions needed for this reaction.

(ii) State the *type of reaction* occurring here.

One of the steps during this reaction is the following process.

$$I^{\cdot} + CH_3CH_3 \rightarrow HCl + CH_3CH_2^{\cdot}$$

(iii) Use the Data Booklet to calculate the enthalpy change, ΔH of this step.

(iv) Use the Data Booklet to calculate the enthalpy change, ΔH, of the similar reaction:

$$Cl^{\cdot} + CH_3CH_3 \rightarrow HI + CH_3CH_2^{\cdot}$$

(v) Hence suggest why it is not possible to make iodoethane by reacting together iodine and ethane.

(vi) Complete the following equations of some possible steps in the formation of chloroethane.

$Cl_2 \rightarrow$ …….

$Cl^{\cdot} + CH_3CH_3 \rightarrow HCl + CH_3CH_2^{\cdot}$

$CH_3CH_2^{\cdot}$ + ……. → …….. + ……

……. + ……..→ CH_3CH_2Cl

[8]

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