

PROSPERITY ACADEMY

AS CHEMISTRY 9701

Crash Course

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HALOGENOALKANES

COMPLETE NOTES



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Halogenoalkanes: - Organic compounds in which one or more of the hydrogen atoms are replaced by a halogen (F, Cl, Br, I)

→ Primary halogenoalkanes: - Halogenoalkanes in which the C atom carrying the halogen is bonded to only 1 alkyl group (has 2 H)



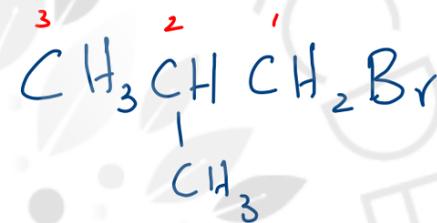
iodoethane



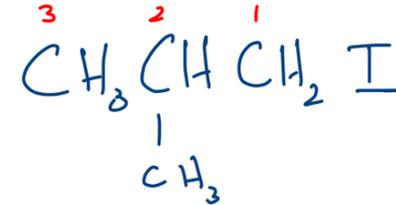
bromoethane



1-chloropropane

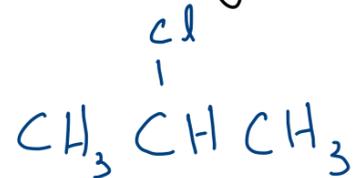


1-bromo-2-methylpropane

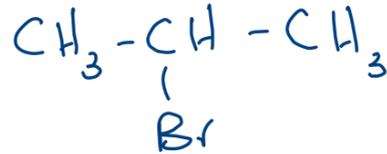


1-iodo-2-methylpropane

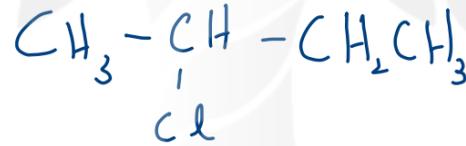
→ Secondary halogenoalkane: - Halogenoalkanes in which the C atom carrying the halogen is bonded to 2 alkyl groups (has 1 H)



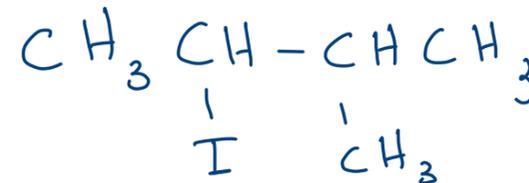
2-chloropropane



2-bromopropane

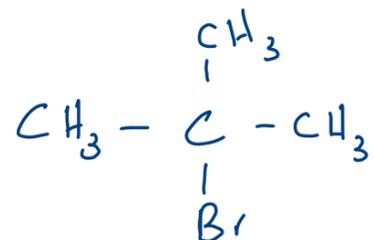


2-chlorobutane

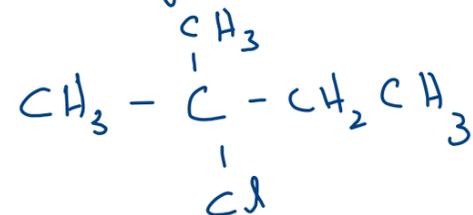


2-iodo-3-methylbutane

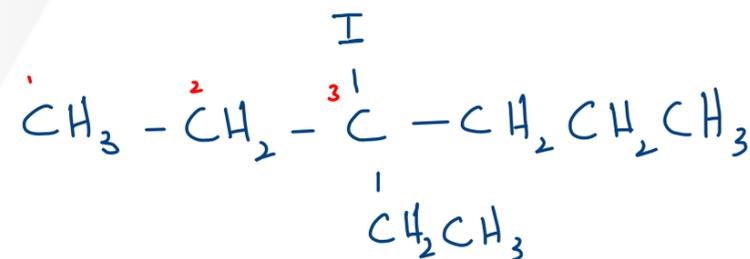
→ Tertiary halogenoalkane: - Halogenoalkanes in which the C atom carrying the halogen is bonded to 3 alkyl groups (has 0 H)



2-bromo-2-methylpropane



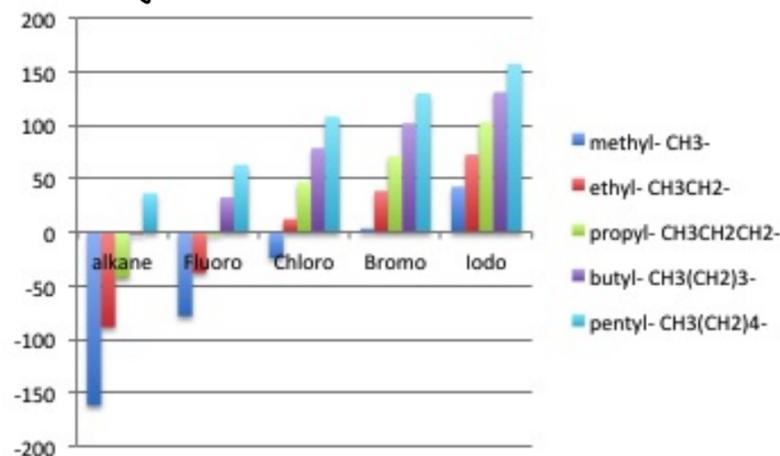
2-chloro-2-methylbutane



3-ethyl-3-iodohexane

Physical Properties:-

Boiling points



- Halogenoalkanes have higher b.p than alkanes:-

- Halogenoalkanes have more no. of e⁻ so they have stronger temporary dipoles (CH₄: 16, CH₃F: 24, CH₃Cl: 32)
- Bonds such as C-F and C-Cl and C-Br are polar so halogenoalkanes also have permanent dipoles

- Boiling points increase as C chain length increases:-

- More no. of e⁻ → Stronger temporary dipoles

- The boiling points of halogenoalkanes increase from F → Cl → Br → I.

- More no. of e⁻ → Stronger temporary dipoles (CH₃F: 24, CH₃Cl: 32, CH₃Br: 50, CH₃I: 68)

- F → Cl → Br → I: electronegativity decreases → bond polarity decreases → permanent dipole forces ↓

(C and H and I have same electronegativity)

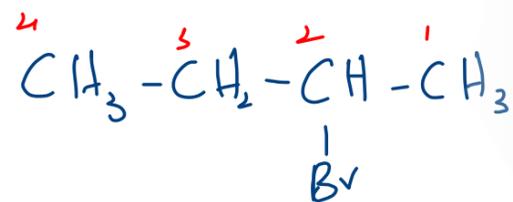
the no. of e⁻ is so much that it outweighs the permanent dipole forces ↓

- Halogenoalkanes containing F and Cl might be soluble as they will be polar → hydrogen bond to water

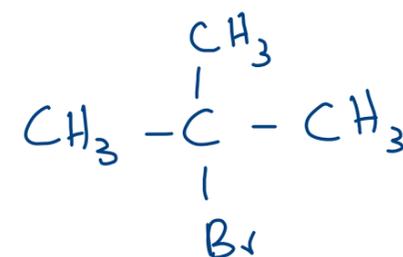
Boiling point of isomers



primary
1-bromo butane



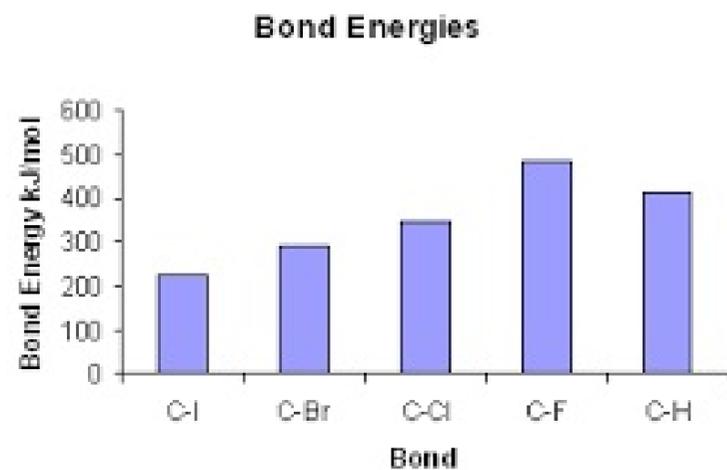
secondary
2-bromo butane



tertiary
2-bromo-2-methyl propane

B.p. decrease because branched isomers cannot pack as closely. →

Chemical properties:-



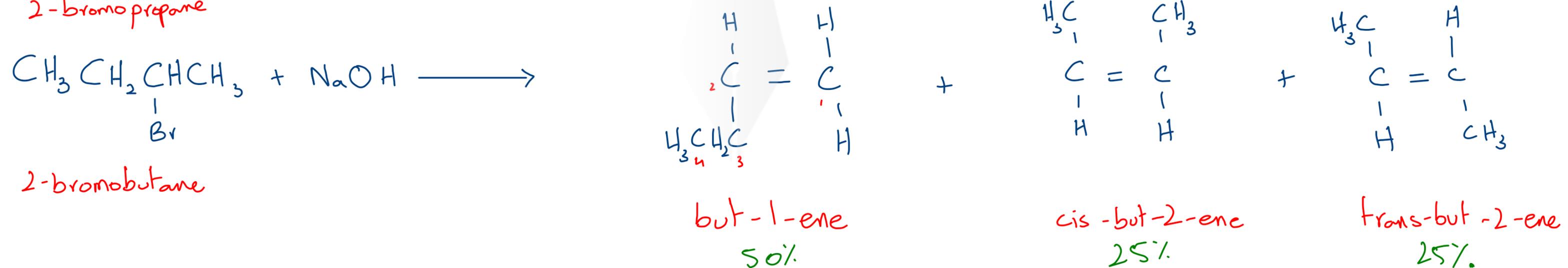
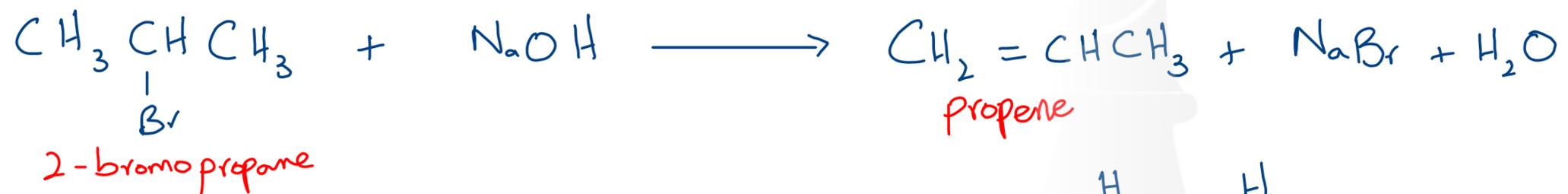
- Bond energies decrease from $C-F \rightarrow C-Cl \rightarrow C-Br \rightarrow C-I$:-

- 1) Smaller halogens have more efficient orbital overlap
- 2) $C-F \rightarrow C-I$: bond polarity decreases

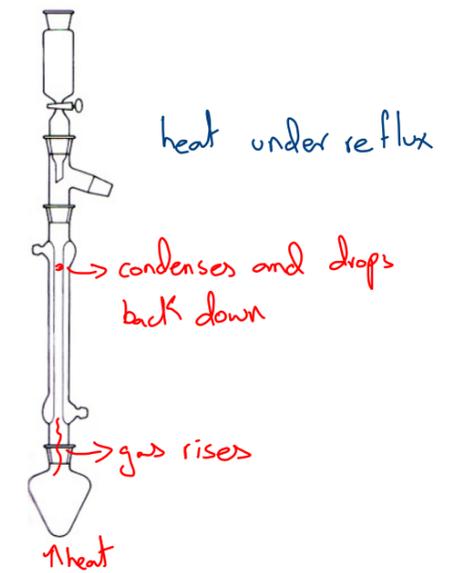
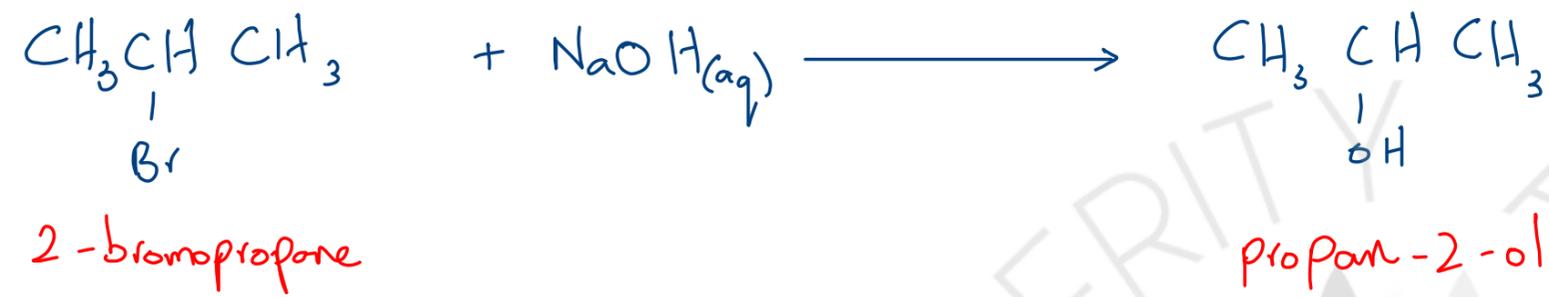
- Order of reactivity: $C-F \rightarrow C-Cl \rightarrow C-Br \rightarrow C-I$
 lowest highest
↑ reactivity increases

Reactions of Halogenoalkanes:-

1) Elimination:- Ethanolic NaOH or KOH, heat under reflux

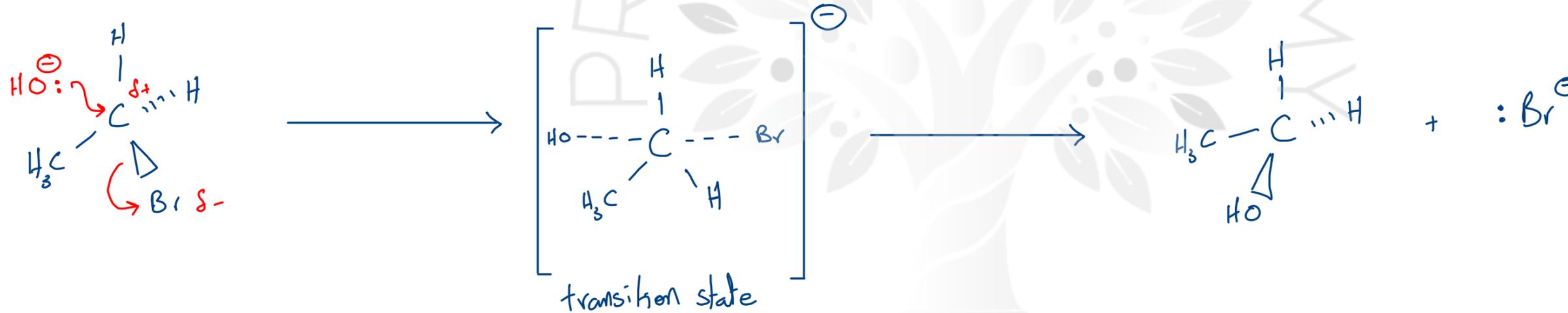


2) Substitution reactions:- Substitution of OH group - Aqueous NaOH or KOH, heat under reflux

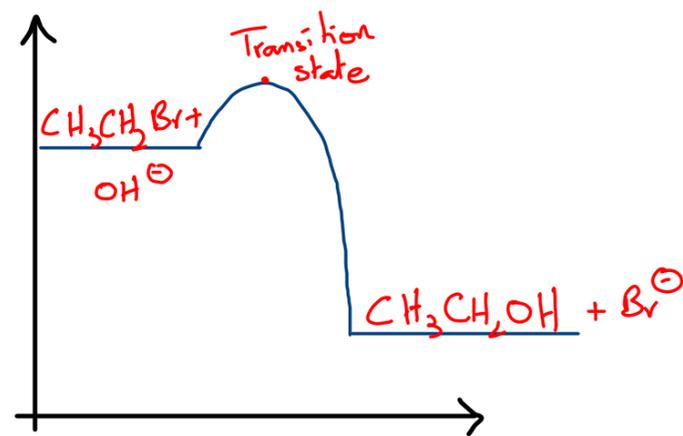


Mechanism:- Nucleophilic substitution
Nucleophile:- A species that donates a pair of electrons

S_N2 (Bimolecular Nucleophilic substitution) Mechanism:- Substitution in primary halogenoalkanes happens this way

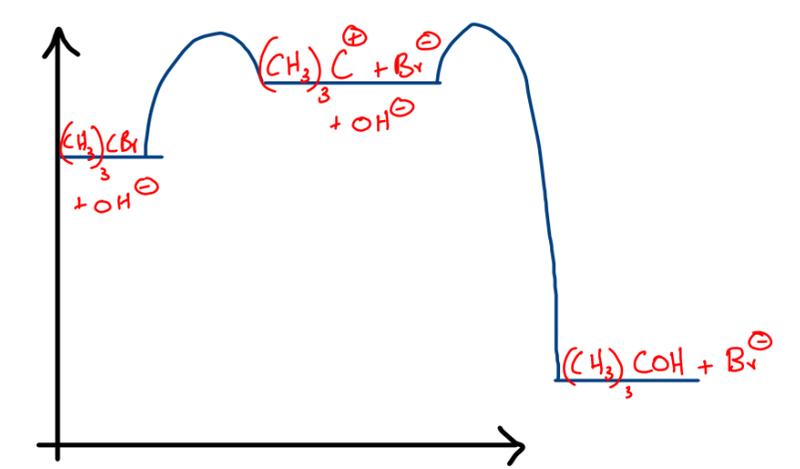
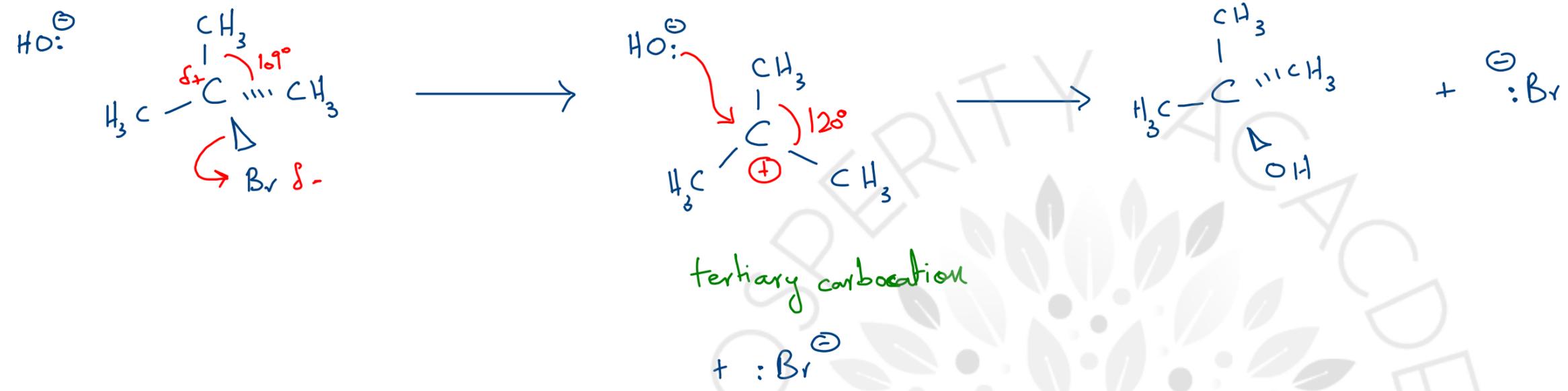


- The OH^- acts as a nucleophile and uses its lone pair to attack the δ^+ C atom from opposite the leaving group.



- Primary halogenoalkanes do not undergo S_N1 mechanism as they only have 1 alkyl group which cannot stabilise it.

S_N1 (Unimolecular nucleophilic substitution) Mechanism:- Substitution in tertiary halogenoalkanes happens this way



- The slowest rate determining step is the first one
- The carbocation formed is a tertiary carbocation and so was stabilised by the positive inductive effect \rightarrow This cannot happen for primary halogenoalkanes
- Tertiary halogenoalkanes don't undergo S_N2 mechanism as the large alkyl groups prevent OH^- from attacking, this is known as steric hindrance.

Checking the halogen in a halogenoalkane:- $NaOH(aq) + \text{heat} + \text{dil. } HNO_3 + AgNO_3 \rightarrow$ The corresponding silver halide salt is made

Salt	Precipitate
$AgCl$	white ppt
$AgBr$	cream ppt
AgI	yellow ppt

\rightarrow To confirm use $NH_3(aq)$
 \rightarrow dissolves in dil $NH_3(aq)$
 \rightarrow precipitate takes too long to form
 \rightarrow dissolves in conc. $NH_3(aq)$
 \rightarrow precipitate takes some time to form
 \rightarrow does not dissolve
 \rightarrow precipitate formed immediately

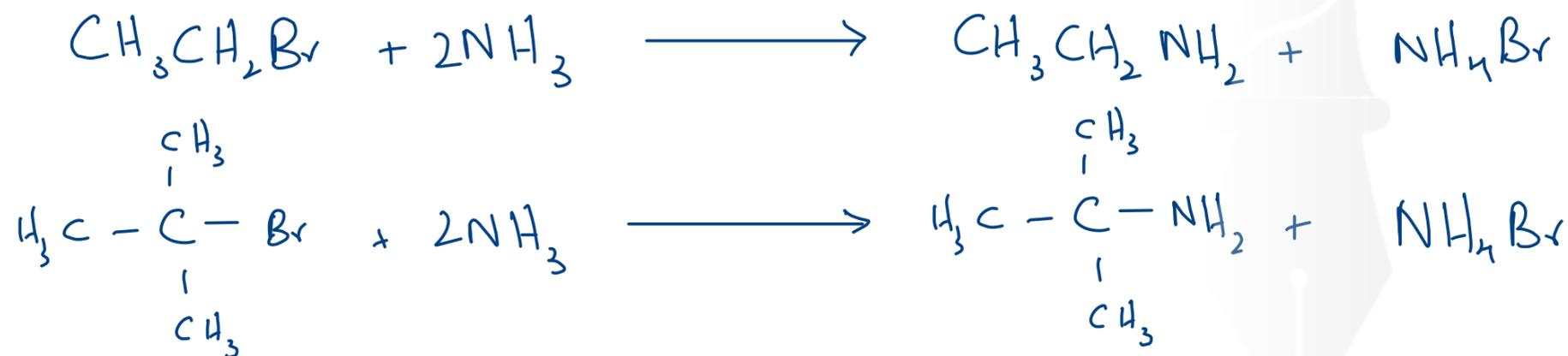
bond energy highest
 bond energy lowest

Trend in giving precipitate by tertiary, secondary, primary halogenoalkane: — $\overset{\text{fastest}}{\text{Tertiary}} \longrightarrow \overset{\text{moderate}}{\text{secondary}} \longrightarrow \overset{\text{slowest}}{\text{primary}}$
→
time increases

- The tertiary halogenoalkane itself releases the halide ion and is then stabilised by the positive inductive effect of alkyl groups until a OH^\ominus attacks.
- The primary halogenoalkane takes longer as it cannot release a halide ion itself and needs an OH^\ominus to attack.

2) Substitution reactions:— Substitution of NH_2 — ethanolic NH_3 in a sealed tube under pressure + heat
not water as OH would substitute instead of NH_2
 NH_3 is less dense than air so it would rise up the condenser and not react.

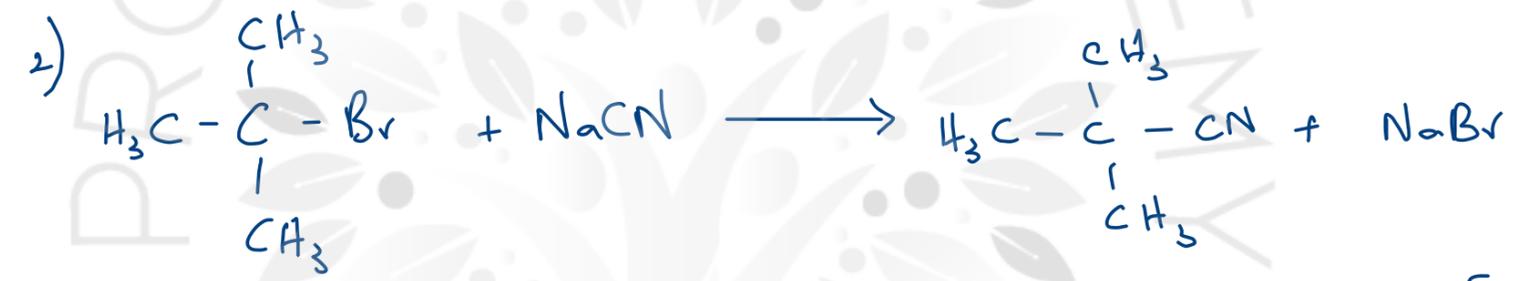
- A primary amine and ammonium salt is produced.





2) Substitution reactions:- Substitution of CN — NaCN or KCN dissolved in ethanol + heat under reflux
 otherwise OH^- would substitute

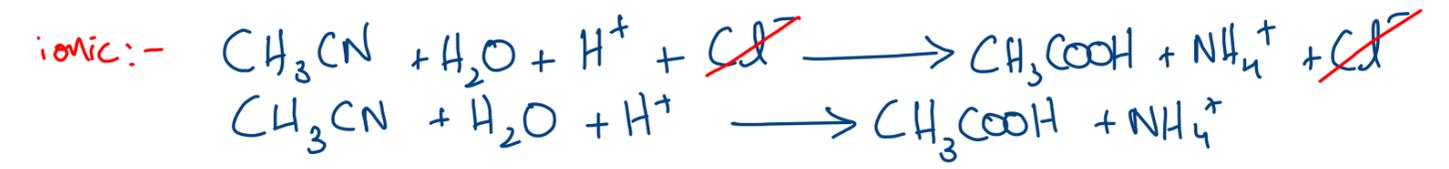
- A nitrile is produced



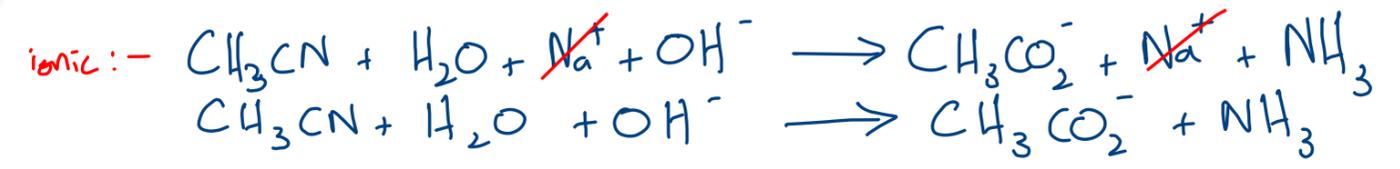
- This reaction is important as this lengthens the carbon chain

- We can hydrolyse the CN to COOH.

1) Acid (dil. HCl or H_2SO_4) + heat under reflux

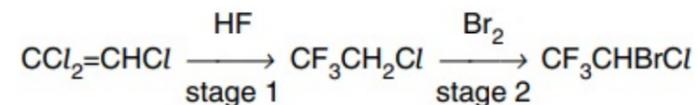


2) Alkali (dil. NaOH) + heat under reflux



- Add dil HCl to make carboxylate salt into acid

1 The anaesthetic *halothane*, CF_3CHBrCl , is made industrially as shown below.



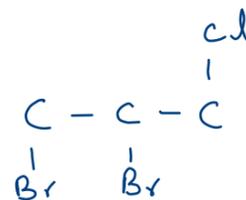
What type of reaction is occurring in stage 2?

- A electrophilic addition
- B electrophilic substitution
- C** free radical substitution
- D nucleophilic addition

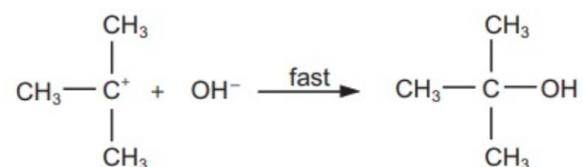
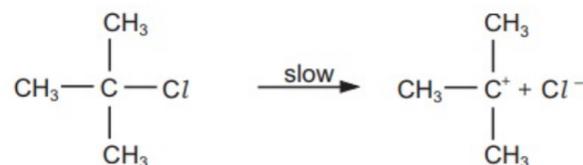
5 1,2-Dibromo-3-chloropropane (DBCP) has been used in the control of earthworms in agricultural land.

What would be the best synthesis of this compound?

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + 2\text{Br}_2 \rightarrow \text{DBCP} + 2\text{HBr}$ *free radical substitution*
- B $\text{CH}_3\text{CHBrCH}_2\text{Br} + \text{Cl}_2 \rightarrow \text{DBCP} + \text{HCl}$ *free radical substitution*
- C** $\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{Br}_2 \rightarrow \text{DBCP}$ *electrophilic addition*
- D $\text{ClCH}_2\text{CH}=\text{CH}_2 + \text{PBr}_5 \rightarrow \text{DBCP} + \text{PBr}_3\text{X}$

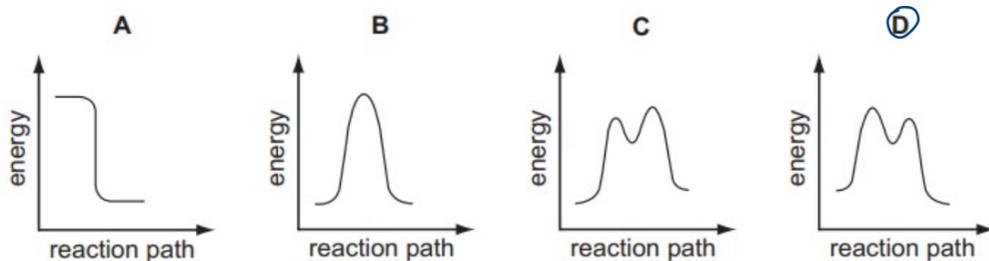


6 A possible mechanism of the hydrolysis of 2-chloro-2-methylpropane is shown.



S_N1

Which diagram represents the reaction profile for this mechanism?



10 Dichlorodifluoromethane, CCl_2F_2 , has been used in aerosol propellants and as a refrigerant.

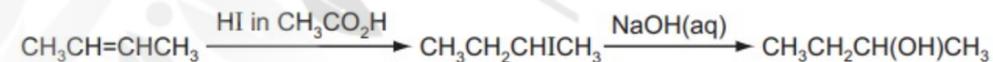
Which statement helps to explain why dichlorodifluoromethane is chemically inert?

- A** The carbon-fluorine bond energy is large.
- B The carbon-fluorine bond has a low polarity.
- C Fluorine is highly electronegative.
- D Fluorine compounds are non-flammable.

20 Which compound undergoes an $\text{S}_{\text{N}}1$ substitution reaction?

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ *primary*
- B $(\text{CH}_3)_3\text{CCH}_2\text{I}$ *primary*
- C** *tertiary*
- D $\text{CH}_2=\text{CHCl}$

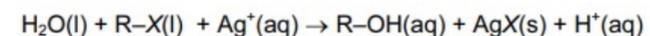
21 Which pair of reaction types is illustrated by the reaction sequence below?



- A electrophilic addition and electrophilic substitution
- B** electrophilic addition and nucleophilic substitution
- C nucleophilic addition and electrophilic substitution
- D nucleophilic addition and nucleophilic substitution

23 Four drops of 1-chlorobutane, 1-bromobutane and 1-iodobutane were put separately into three test-tubes containing 1.0 cm^3 of aqueous silver nitrate at 60°C .

A hydrolysis reaction occurred. (R represents the butane chain C_4H_9- and X the halogen atom.)



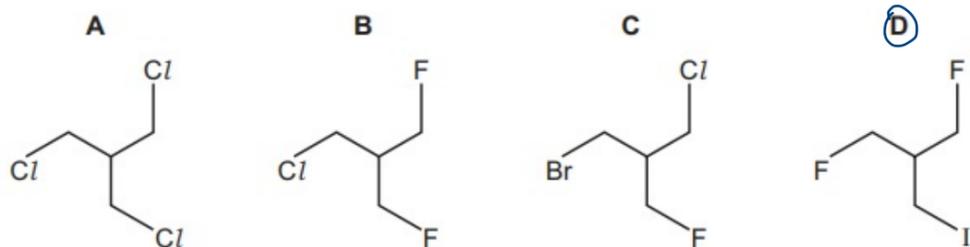
The rate of formation of cloudiness in the tubes was in the order $\text{RCI} < \text{RBr} < \text{RI}$.

Why is this?

- A The R-X bond polarity decreases from RCI to RI .
- B The solubility of AgX(s) decreases from AgCl to AgI .
- C The ionisation energy of the halogen decreases from Cl to I .
- D** The bond energy of R-X decreases from RCI to RI .

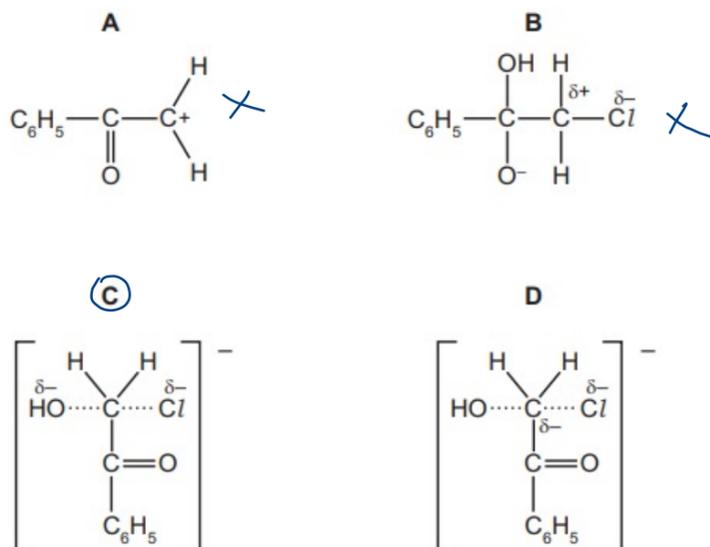
30 The presence of halogen in an organic compound may be detected by warming the organic compound with aqueous silver nitrate.

Which compound would produce a precipitate quickest?



31 When phenacyl chloride, $C_6H_5COCH_2Cl$, is reacted with aqueous NaOH, the substitution reaction follows an S_N2 mechanism. (negative intermediate \rightarrow transition state)

Which structure represents a species formed during the reaction?



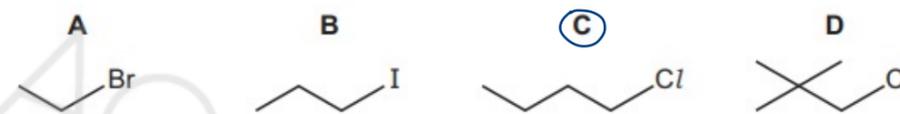
34 Aqueous sodium hydroxide reacts with 1-bromopropane to give propan-1-ol.

How should the first step in the mechanism be described?

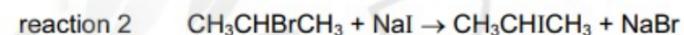
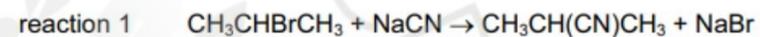
- A** by a curly arrow from a lone pair on the OH^- ion to the $C^{\delta+}$ atom of 1-bromopropane
B by a curly arrow from the $C^{\delta+}$ atom of 1-bromopropane to the OH^- ion
C by a curly arrow from the $C-Br$ bond to the C atom
D by the homolytic fission of the $C-Br$ bond

36 Compound Y can be hydrolysed by warm aqueous silver nitrate to form a precipitate that is soluble in dilute aqueous ammonia. Compound Y can undergo an elimination reaction to form an alkene.

What could be the skeletal formula of compound Y?



41 Under identical conditions, even though it proceeds by the same mechanism, reaction 1 is faster than reaction 2.

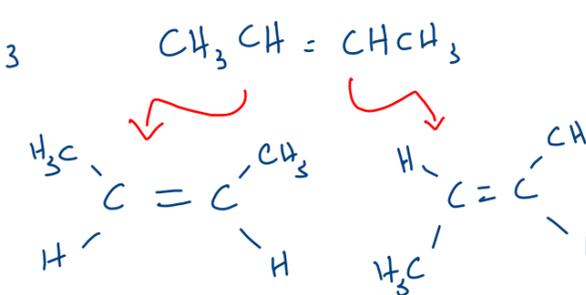


What factor will explain this result?

- A** The $C-I$ bond is a stronger bond than the $C-Br$ bond. \times
B The $C-N$ bond is a stronger bond than the $C-I$ bond. \times
C The cyanide ion is a stronger nucleophile than the iodide ion. \checkmark
D The cyanide ion is a weaker nucleophile than the iodide ion.

47 Including structural and stereoisomers, how many isomeric products are produced when alcoholic KOH reacts with 2-chlorobutane?

- A** 1 **B** 2 **C** 3 **D** 4



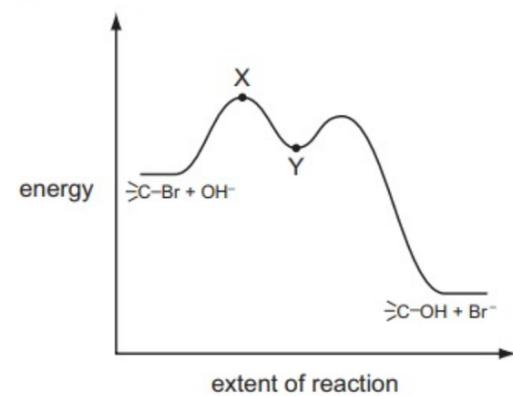
57 2-bromopropane reacts with a hot concentrated solution of sodium hydroxide in ethanol.

Which substance is the major product of this reaction?

- A** propan-1-ol
B propan-2-ol
C 2-hydroxypropene
D propene



- 64 A tertiary bromoalkane, indicated here by >C-Br , reacts with aqueous NaOH. The mechanism has the reaction pathway below.



Which point in the diagram is correctly identified?

A X is >C^+

B X is $\left[\text{HO} \cdots \text{C} \cdots \text{Br} \right]^-$

C Y is >C^+

D Y is $\left[\text{HO} \cdots \text{C} \cdots \text{Br} \right]^-$

- 69 Structural isomerism and stereoisomerism should be considered in answering this question.

Compound J is reacted with KOH dissolved in ethanol. Three isomeric alkenes with molecular formula C_4H_8 are formed.

What is J?

A $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—Br}$

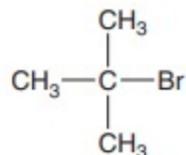
B $\begin{array}{c} \text{CH}_3\text{—CH—CH}_2\text{—CH}_3 \\ | \\ \text{Br} \end{array}$

C $\begin{array}{c} \text{CH}_3\text{—CH—CH}_2\text{—Br} \\ | \\ \text{CH}_3 \end{array}$

D $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{—C—Br} \\ | \\ \text{CH}_3 \end{array}$



1-bromobutane



2-bromo-2-methylpropane

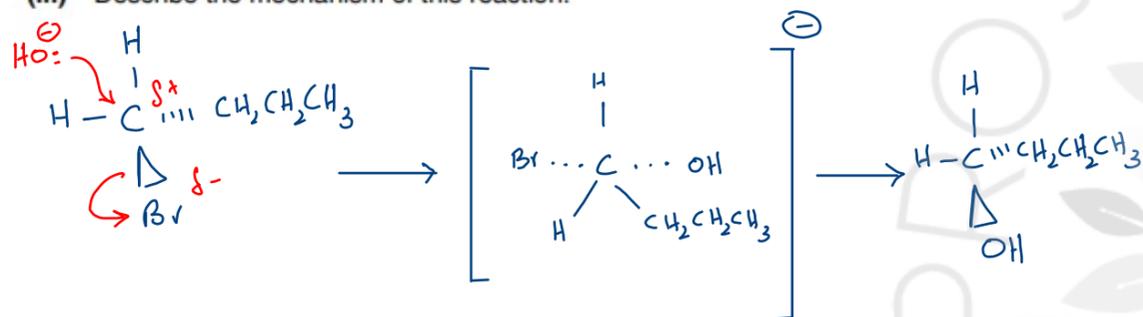
(a) 1-Bromobutane reacts with **aqueous** sodium hydroxide to form butan-1-ol.

(i) Give a balanced equation for this reaction.



(ii) Name the type of reaction. *Nucleophilic substitution*

(iii) Describe the mechanism of this reaction.



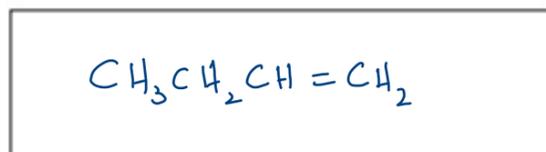
[5]

(b) 1-Bromobutane and 2-bromo-2-methylpropane both react with an **ethanolic (alcoholic)** solution of sodium hydroxide to form alkenes.

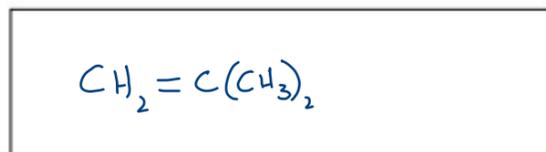
(i) Name the type of reaction. *elimination*

(ii) Identify, by means of the structural formula, the alkene formed from

I 1-bromobutane,



II 2-bromo-2-methylpropane.



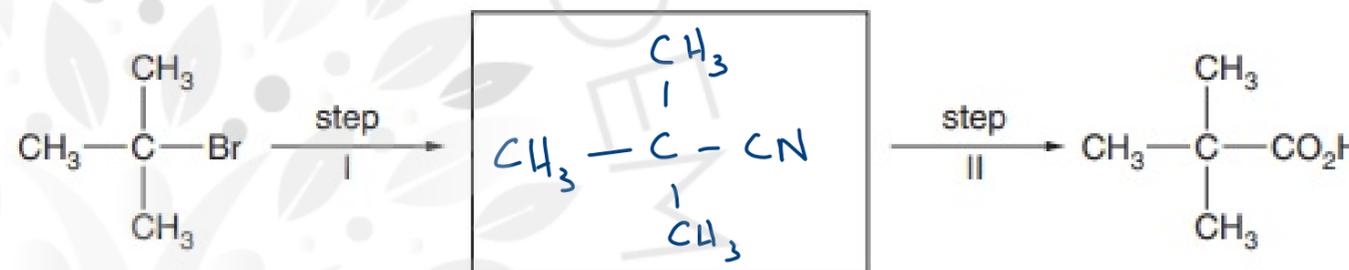
(iii) Hot, concentrated manganate(VII) ions break the double bond in alkenes. Each of the two alkenes in (b)(ii) gives CO_2 and H_2O from the terminal group, but the rest of the molecule remains as an organic oxidation product. Suggest the formula of each of these products.

from I *$\text{CH}_3\text{CH}_2\text{COOH}$*

from II *CH_3COCH_3*

[5]

(c) Complete the reaction sequence giving the intermediate, the reagents and the conditions for the synthesis of 2,2-dimethylpropanoic acid.



Step I: reagent *NaCN in ethanol*

conditions *heat under reflux*

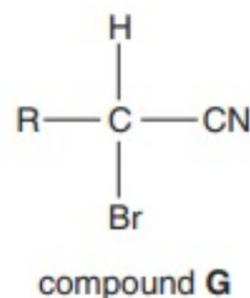
Step II: reagent *dil. H_2SO_4*

conditions *heat under reflux*

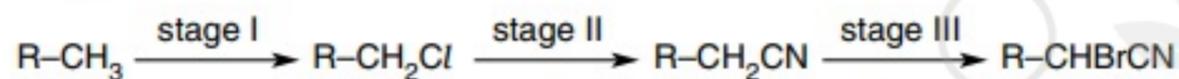
[3]

[Total : 13]

- 4 Compound **G**, in which R- represents the rest of the molecule, was made for use as a tear gas in World War 2.



Compound **G** was made by the following sequence of reactions.



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

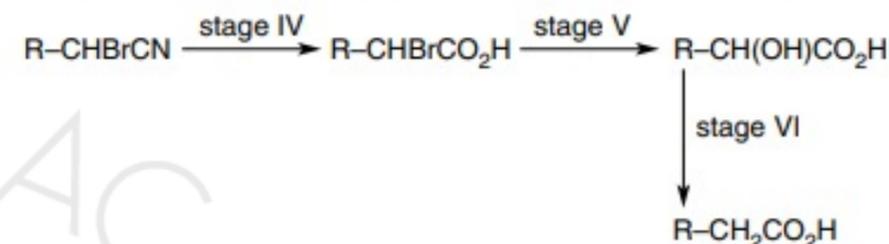
stage I reagent(s) Cl_2 gas
 condition(s) UV light
 stage II reagent(s) NaCN in ethanol
 condition(s) heat under reflux

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

reagent(s) Br_2
 condition(s) U.V. light

[6]

Compound **G** was not actually used in World War 2 and stocks of it had to be destroyed safely. The following sequence of reactions was used in this process.



- (b) For stage IV and for stage V state the reagent(s) and condition(s) necessary to bring about each reaction.

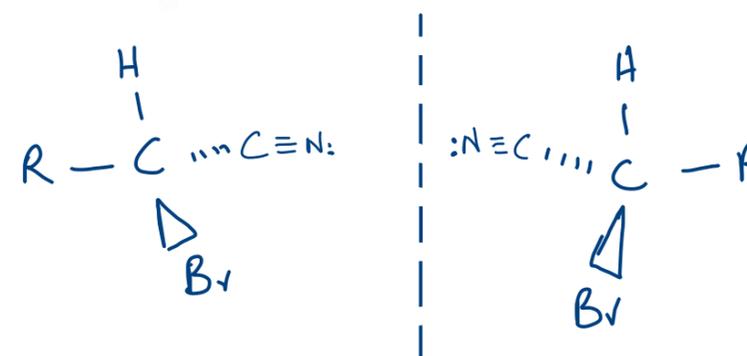
stage IV reagent(s) dil H_2SO_4
 condition(s) heat under reflux
 stage V reagent(s) NaOH dissolved in water
 condition(s) heat under reflux [4]

- (c) The full sequence of stages I to VI involves some compounds which contain chiral centres.

- (i) Explain what is meant by the term *chiral centre*.

A carbon atom that is bonded to 4 other atoms or group of atoms.

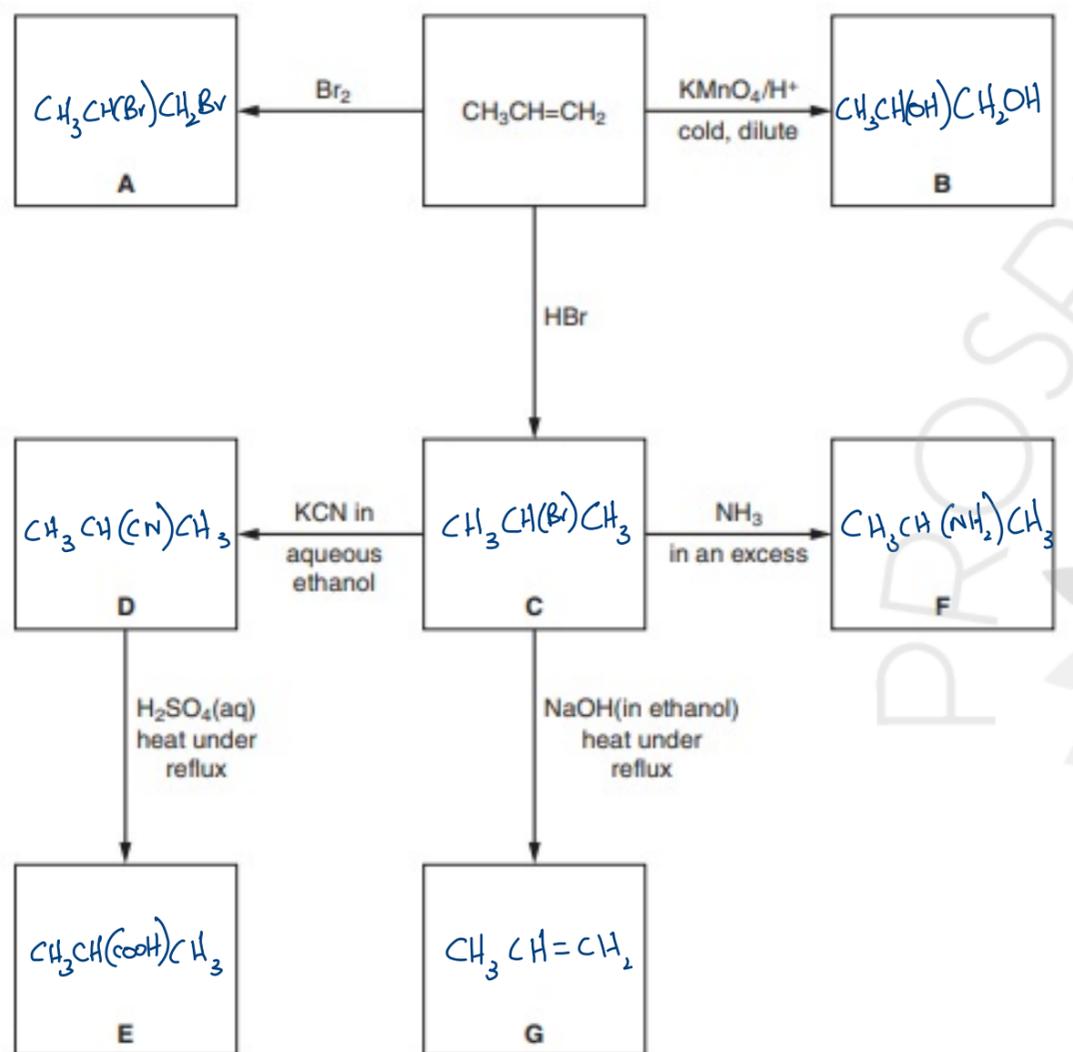
- (ii) Draw displayed formulae for the isomers of **one** compound in the full sequence of stages I to VI which you consider to be chiral.



[3]

[Total: 13]

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



- (b) Under suitable conditions, compound **E** will react with compound **B**.

(i) What functional group is produced in this reaction?

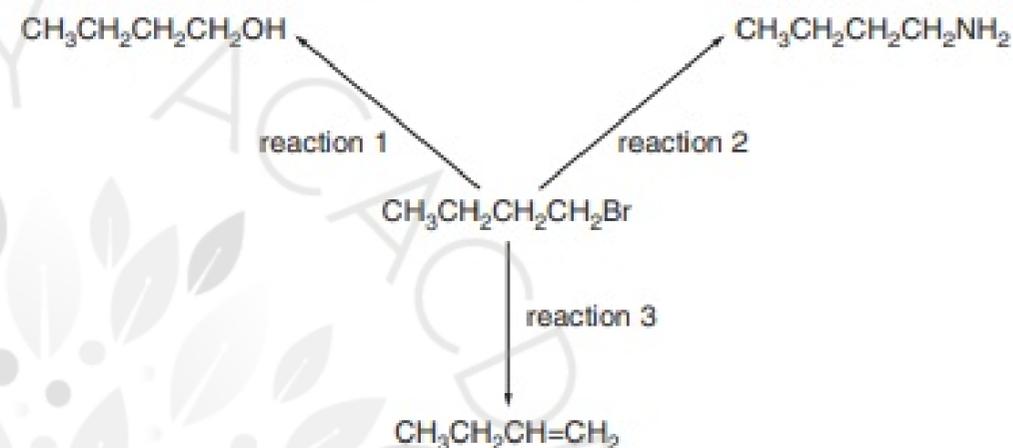
(ii) How is this reaction carried out in a school or college laboratory?

[7]

[3]

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

Three reactions of 1-bromobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, are shown below.



- (a) For each reaction, state the reagent and solvent used.

reaction 1 reagent NaOH
solvent water

reaction 2 reagent NH_3
solvent ethanol

reaction 3 reagent NaOH
solvent ethanol

[6]

- (b) When 1-iodobutane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$, 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 reaction of 1-bromobutane?

~~Use appropriate data from the Data Booklet to explain your answer.~~

The C-I bond energy is less than the C-Br bond and so it breaks much more easily so the reaction rate will be faster for 1-iodobutane

[3]

- 8 Although few halogenoalkanes exist naturally, such compounds are important as intermediates in organic reactions and as solvents.

The bromoalkane **B** has the following composition by mass: C, 29.3%; H, 5.7%; Br, 65.0%.
The relative molecular mass of **B** is 123.

- (a) Calculate the molecular formula of **B**.

$$n = \begin{array}{ccc} \text{C} & \text{H} & \text{Br} \\ \hline 29.3 & 5.7 & 65 \\ 12 & 1 & 79.9 \end{array}$$

$$(2.44167 : 5.7 : 0.81352) \times 0.81352$$

$$3 : 7 : 1$$

$$\text{Emp formula} = \text{C}_3\text{H}_7\text{Br}$$

$$Mr = 122.9$$

$$n = \frac{123}{122.9} \approx 1$$

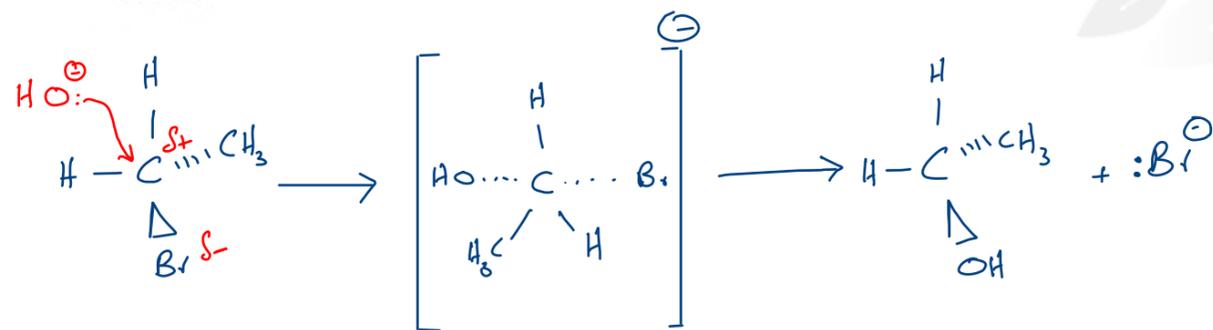
$$\text{molecular formula} = \text{C}_3\text{H}_7\text{Br}$$

[3]

Halogenoalkanes such as bromoethane, $\text{C}_2\text{H}_5\text{Br}$, have two different reactions with sodium hydroxide, NaOH, depending on the conditions used.

- (b) (i) When hot aqueous NaOH is used, the $\text{C}_2\text{H}_5\text{Br}$ is hydrolysed to ethanol, $\text{C}_2\text{H}_5\text{OH}$.

Describe the mechanism of this reaction. In your answer, show any relevant charges, dipoles, lone pairs of electrons and movement of electron pairs by curly arrows.



- (ii) What will be formed when $\text{C}_2\text{H}_5\text{Br}$ is reacted with NaOH under different conditions?

ethene + HBr

- (iii) What are the conditions used?

ethanolic NaOH + heat under reflux

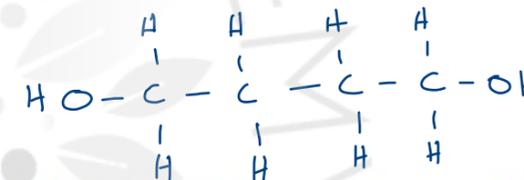
- (iv) What type of reaction is this?

elimination

[7]

When 1,4-dichlorobutane, $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$, is reacted with NaOH, two different reactions can occur, depending on the conditions used.

- (c) (i) Draw the **displayed** formula of the product formed when 1,4-dichlorobutane is reacted with hot aqueous NaOH as in (b)(i).



- (ii) Draw the **skeletal** formula of the product formed when 1,4-dichlorobutane is reacted with NaOH in the way you have described in (b)(ii) and (b)(iii).



[2]