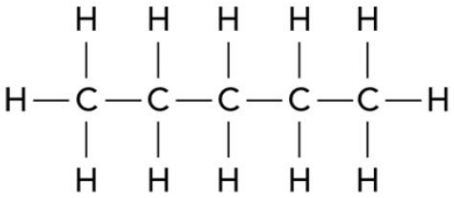
Hydrocarbons

Review



displayed formula of pentane

$CH_3CH_2CH_2CH_2CH_3$

structural formula of pentane

skeletal formula of pentane

The three steps in a free-radical reaction are:
initiation step: the formation of free radicals to start a reaction off
propagation steps: steps in a mechanism that regenerate more free radicals
termination step: the final step in a mechanism, when two free radicals meet and form a product molecule.

eg: $CH_4 + Cl_2 \xrightarrow[light]{UV} CH_3Cl + HCl$

initiation: $Cl_2 \xrightarrow[light]{UV} 2\,Cl\bullet$ (homolytic fission)

propagation: $CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl$

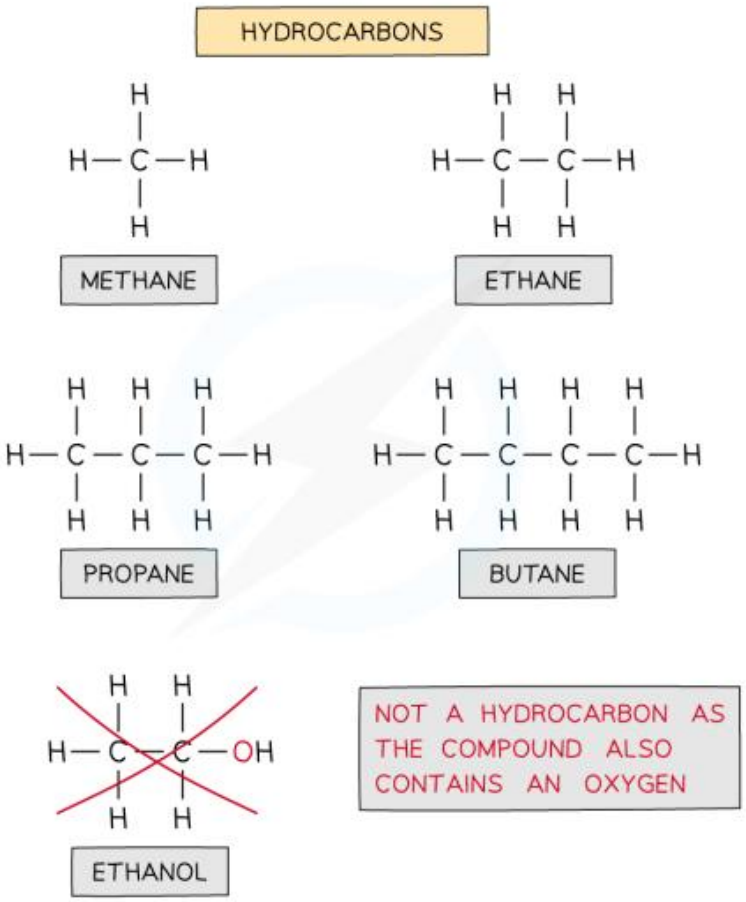
$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$

termination: $\bullet Cl + \bullet CH_3 \longrightarrow CH_3Cl$

$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$

Hydrocarbons

- Hydrocarbons are compounds that are made up of carbon and hydrogen atoms **ONLY**



1.The homologous group of alkanes

The general formula for the alkanes is C_nH_{2n+2}

Alkane molecules are non-polar, so they are not attacked by nucleophiles or electrophiles. They have no partial positive charges (δ+) on any of their carbon atoms to attract nucleophiles, neither do they have areas of high electron density to attract electrophiles

2.Combustion of alkanes

$$\text{alkane} + \text{oxygen} \xrightarrow{\text{complete combustion}} \text{carbon dioxide} + \text{water}$$

complete combustion

A sample of propane, C_3H_8, with a mass of 9.61 g is completely combusted in an excess of oxygen under room conditions.

Which volume of carbon dioxide gas is produced?

A. 4.89 dm^3
B. 5.24 dm^3
C. 14.7 dm^3
D. 15.7 dm^3

$C_3H_8 + O_2 \rightarrow 3CO_2\ 4H_2O$

$12 \times 3 + 8 = 44$

36

$0.218mol \times 3 = 0.655$

44 18

On complete combustion, a sample of X produces 44 g of carbon dioxide and 27 g of water.

On complete combustion, a sample of Y produces 44 g of carbon dioxide and 18 g of water.

On complete combustion, a sample of Z produces 22 g of carbon dioxide and 9 g of water.

Which substances could be straight chain alkanes?

1. X ✓
2. Y CH_2 X
3. Z CH_2X

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

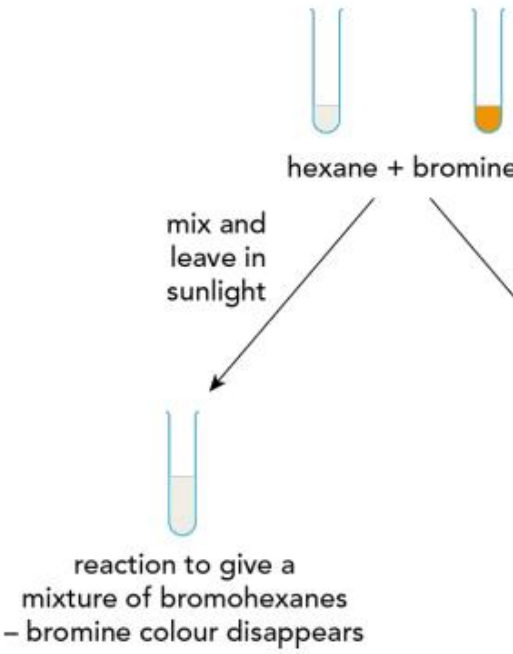
$1\ CO_2 + 1\ H_2O$

C_2H_6

3.Substitution reactions of alkanes

The alkanes will undergo substitution reactions with halogens in sunlight.
Consider the reaction between ethane and chlorine in sunlight:

this type of reaction does not take place in darkness



Initiation

$Br_2 \xrightarrow{UV} \cdot Br + \cdot Br$

propagation

$C_6H_{14} + \cdot Br \rightarrow \cdot C_6H_{13} + H\text{-}Br$

$\cdot C_6H_{13} + Br_2 \rightarrow C_6H_{13}Br + \cdot Br$

Termination

$\cdot C_6H_{13} + \cdot Br \rightarrow C_6H_{13}Br$

$\cdot Br + \cdot Br \rightarrow Br_2$

$\cdot C_6H_{13} + \cdot C_6H_{13} \rightarrow C_{12}H_{26}$

The three steps in a free-radical reaction:
initiation step: the formation of free radicals
propagation steps: regenerate more free radicals
termination step: two free radicals meet and form a product molecule.

Initiation step

The first step in the mechanism is the breaking of the Cl–Cl bond by energy from ultraviolet light in sunlight. This is called the initiation step in the mechanism:

Propagation steps

Free radicals are very reactive. They will attack the normally unreactive alkanes. A chlorine free radical willattack the ethane molecule:

In this propagation step, a C–H bond in CH3CH3 breaks homolytically. An ethyl free radical, ·CH2CH3 , is produced. This can then attack a chlorine molecule, forming chloroethane and regenerating a chlorine free radical:

Termination steps

Whenever two free radicals meet they will react with each other. A single molecule is the only product. As no free radicals are made that can carry on the reaction sequence, the chain reaction stops. Examples of termination steps include:

Which free radicals can be generated during a free-radical substitution reaction between chlorine and ethane?

1. $CH_3\bullet$
2. $CH_2ClCH_2\bullet$
3. $CH_3CCl_2\bullet$

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

During the bromination of methane, the free radical $CH_3\bullet$ is generated. A possible termination step of this reaction is the formation of C_2H_6 by the combination of two free radicals.

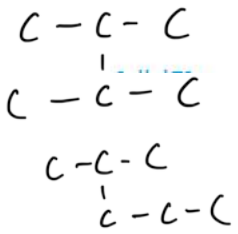
What could be produced in a termination step during the bromination of **propane**?

1. $CH_3CH_2CH(CH_3)CH_2CH_3$
2. $CH_3CH(CH_3)CH(CH_3)_2$
3. $CH_3CH_2CH_2CH(CH_3)_2$

A. 1, 2 and 3 are correct
B. 1 and 2 only are correct
C. 2 and 3 only are correct
D. 1 only is correct

C_3H_8

C_6H_{14}



Which equation represents a valid propagation step in the chlorination of ethane?

A. $C_2H_6 + Cl\bullet \rightarrow C_2H_5Cl + H\bullet$
B. $C_2H_5Cl + Cl\bullet \rightarrow C_2H_4Cl\bullet + HCl$
C. $C_2H_5Cl + H\bullet \rightarrow C_2H_5\bullet + HCl$
D. $C_2H_5\bullet + Cl\bullet \rightarrow C_2H_5Cl$

Which equation represents the initiation step of the substitution reaction between methane and chlorine?

A. $CH_4 \rightarrow CH_3\bullet + H\bullet$
B. $CH_4 \rightarrow CH_3^- + H^+$
C. $Cl_2 \rightarrow 2Cl\bullet$
D. $Cl_2 \rightarrow Cl^+ + Cl^-$

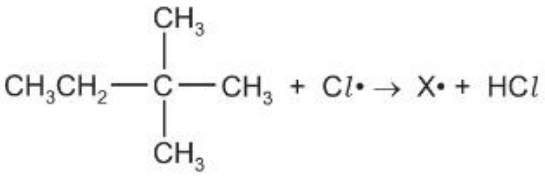
Alkanes are saturated hydrocarbons.

Which type of reaction are alkanes most likely to undergo?

A. electrophilic addition
B. electrophilic substitution
C. free radical substitution
D. nucleophilic addition

When heated with chlorine, the hydrocarbon 2,2-dimethylbutane undergoes free radical substitution.

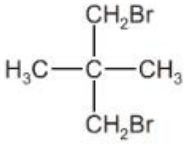
In a propagation step a free radical X• is formed.



How many different structures of X• are possible?

A. 2
B. 3
C. 4
D. 5

The diagram shows the structure of a bromo compound that may be formed by the reaction of bromine with a hydrocarbon.



Which row is correct?

	type of reaction	mechanism
A	addition	electrophilic
B	addition	nucleophilic
C	substitution	nucleophilic
D	substitution	free-radical

4.cracking (Al_2O_3, heat)

When large alkane molecules are cracked, they form smaller alkane molecules and alkene molecules. One possible example of a cracking reaction is:

Equation:

$$C_{10}H_{22} \rightarrow C_5H_{12} + C_5H_{10}$$

$$CH_3(CH_2)_8CH_3 \xrightarrow[\text{heat}]{Al_2O_3} CH_3(CH_2)_4CH_3 + CH_2{=}CHCH_2CH_3$$

$$C_{10}H_{22} \xrightarrow[\text{heat}]{Al_2O_3} C_6H_{14} + C_4H_8$$

5.Combustion of The alkenes

Complete Combustion

Equation:

$$C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2H_2O$$

6.Addition reactions of the alkenes

In these reactions one of the two bonds in the carbon–carbon (C═C) double bond is broken and a new single bond is formed from each of the two carbon atoms.

Hydrogenation, $H_{2(g)}$
Condition: heat, Ni/ Pt

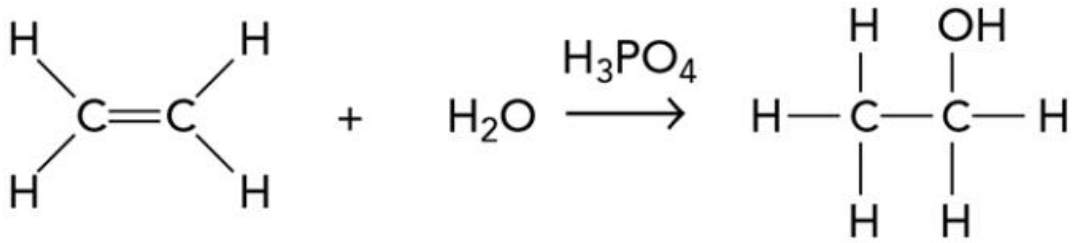
Equation:

When an alkene is bubbled through a concentrated solution of a hydrogen halide (either HF, HCl, HBr or HI) at room temperature, the product is a halogenoalkane. For example:

With longer, asymmetric alkenes there are always two possible products that could be formed. For example, with propene:

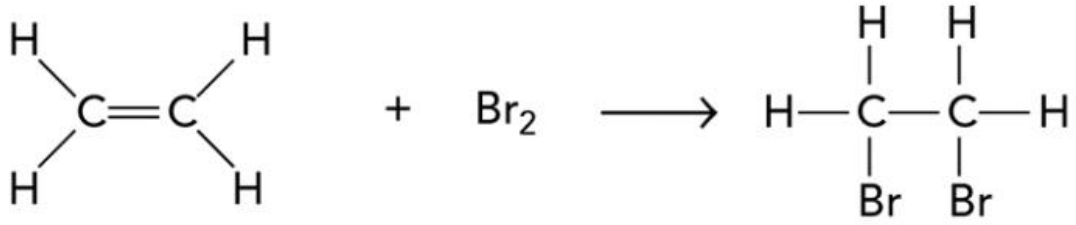
and

Addition of steam, $H_2O(g)$



$$CH_2{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH$$

Addition of halogens, $X_2(aq)$

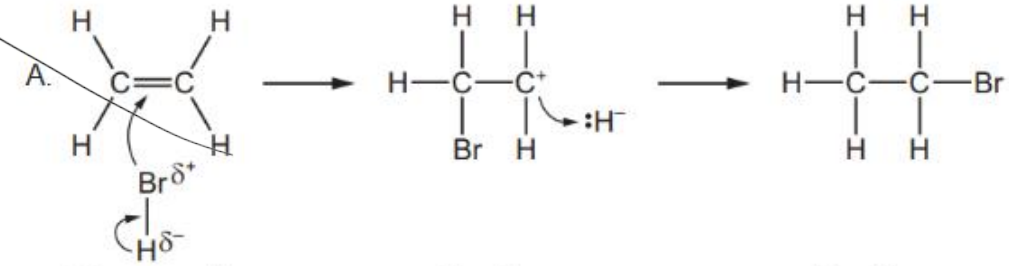


The mechanism of electrophilic addition to alkenes

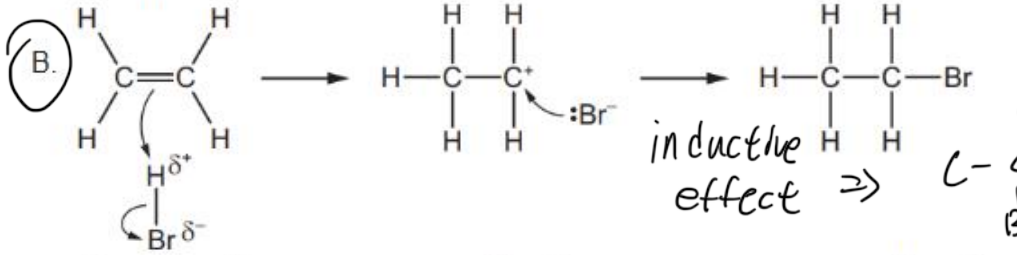
there is an area of high electron density around the C═C bond.

What is the correct mechanism for the addition of hydrogen bromide to ethene?

A.



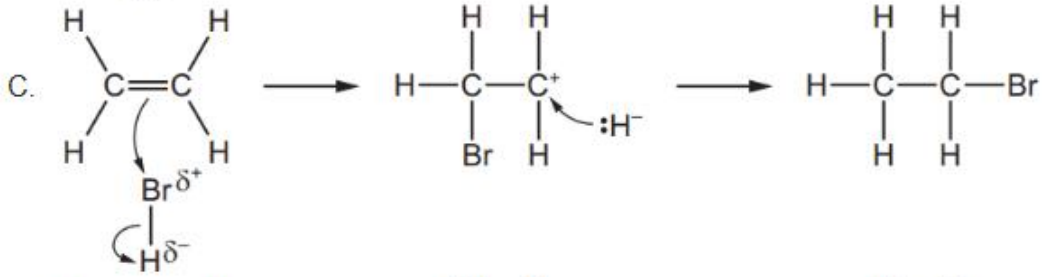
B.



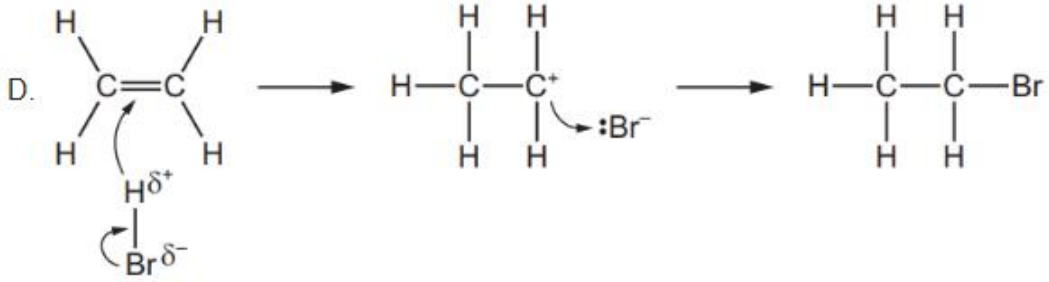
inductive effect ⇒ Major product more stable

C–C(Br)–C(H)

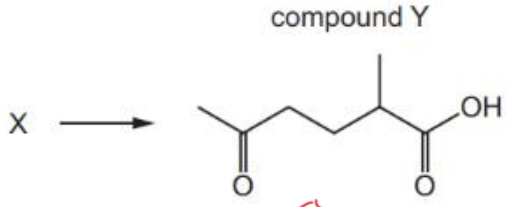
C.



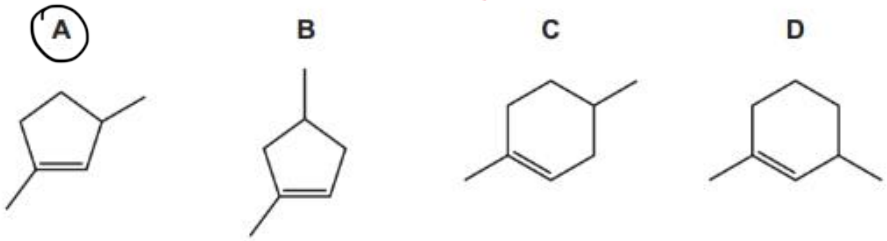
D.



Compound X can be converted into compound Y in a single step.



What could be the identity of X?



Two students each make a statement about 2-methylbut-1-ene.

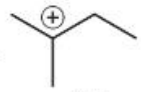
Student 1 states that 2-methylbut-1-ene has geometrical isomers.
Student 2 states that 2-methylbut-1-ene reacts with HBr in an addition reaction to give 1-bromo-2-methylbutane as the main product.

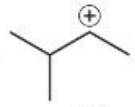
Which students are correct?

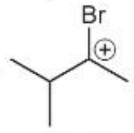
A. both 1 and 2
B. 1 only
C. 2 only
D. neither 1 nor 2

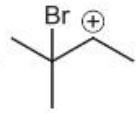
2-methylbut-2-ene reacts with HBr(g) to form two isomeric products. During the reaction two positively charged intermediates can be made.

Which diagram shows the more stable of the two positively charged intermediates?

A. 

B. 

C. 

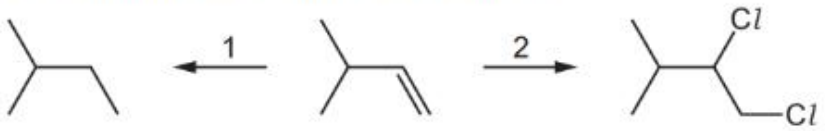
D. 

Propene, bromine and hydrogen bromide are mixed in the dark. A number of products are formed, some in very small quantities.

Which substance will **not** be present in the mixture of products?

A. 1-bromopropane
B. 2-bromopropane
C. 1,1-dibromopropane
D. 1,2-dibromopropane

3-methylbut-1-ene can undergo different types of reaction.



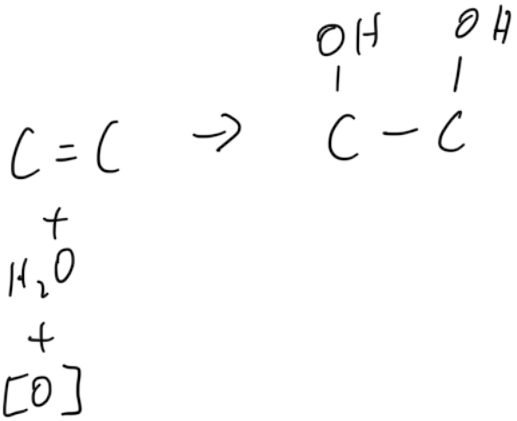
Which row correctly identifies the reaction types?

	reaction 1	reaction 2
A	oxidation	electrophilic addition
B	oxidation	nucleophilic addition
C	reduction	electrophilic addition
D	reduction	nucleophilic addition

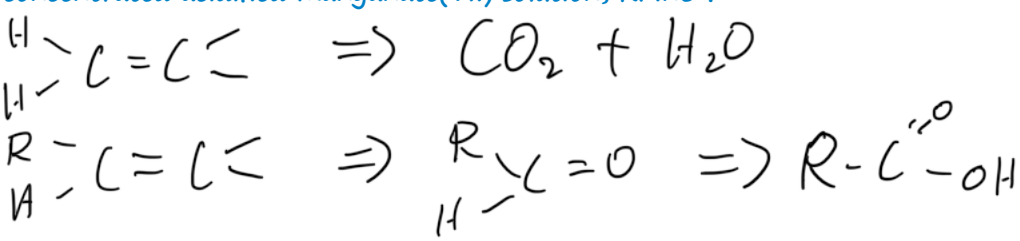
7.Oxidation of the alkenes

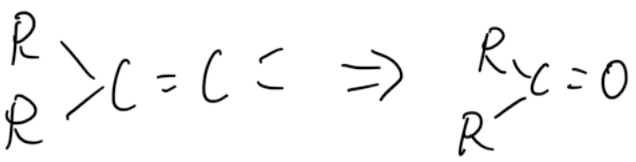
Cold dilute acidified manganate(VII) solution

forming diol



Hot concentrated acidified manganate(VII) solution, KMnO4





The actual products depend on what is bonded to the carbon atoms in the C═C double bond.

We can use this reaction to determine the position of the double bond in larger alkenes. To do this we would need to identify the products of the oxidation reaction and work backwards to deduce the original alkene.

carbon dioxide is given off in the oxidation, this tells us that the double bond was between the end two carbon atoms in the alkene.

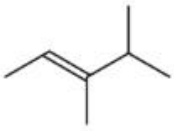
The table describes four reactions of propene.

Which row is correct?

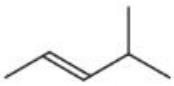
	reagent used	name of main organic product
A	aqueous bromine	2-bromopropane
B	cold acidified aqueous potassium manganate(VII)	propane-1,3-diol
C	hydrogen chloride	2-chloropropane
D	steam	propan-1-ol

Which compound would produce two different carboxylic acids when treated with hot, concentrated, acidified manganate(VII) ions?

A

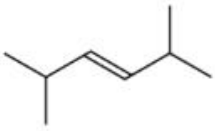


B



C

D

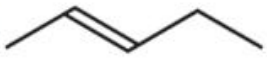


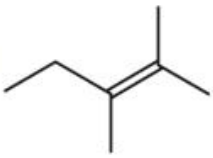
Which substance forms propanoic acid as one of the products when it reacts with hot concentrated acidified potassium manganate(VII)?

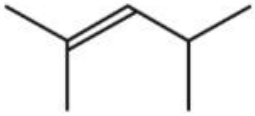
A. but-1-ene
B. but-2-ene
C. 2-methylpropene
D. 2-methylbut-1-ene

Which compound would produce a carboxylic acid and a ketone when treated with hot, concentrated acidified manganate(VII) ions?

A. 

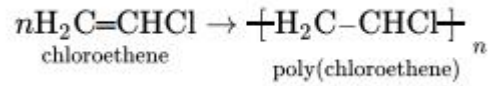
B. 

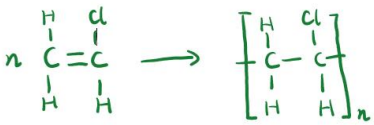
C. 

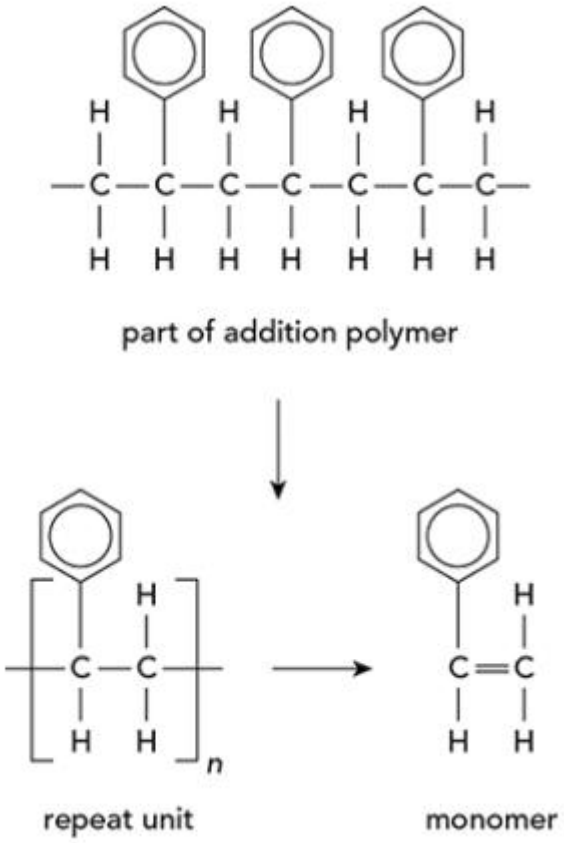
D. 

8. Addition polymerisation

Monomer ⟶ polymer







9. Summary

Alkane (saturated hydrocarbon):

- **Combustion** (complete and incomplete)
- **Free-radical substitution**
- **Cracking** (elimination): alkane → alkene + alkane (no oxygen, high temperature, zeolite catalyst)

Alkene (unsaturated hydrocarbon):

- **Addition** (electrophilic addition):
  - Hydrogen (H_2 (g)): CH2=CH2 + H2 → CH3CH3 (140°C, Ni catalyst)
  - Steam (H2O (g)): CH2=CH2 + H2O → CH3CH2OH (330°C, 6MPa, H3PO4)
  - Hydrogen Halides (HX (aq)): CH2=CH2 + HBr → CH3CH2Br (conc. HX, r.t.p.)
  - Halogens (X2 (aq)): CH2CH2 + Br2 → CH2BrCH2Br (r.t.p.
    - Test for the presence of C=C bond (decolourisation of Br2)

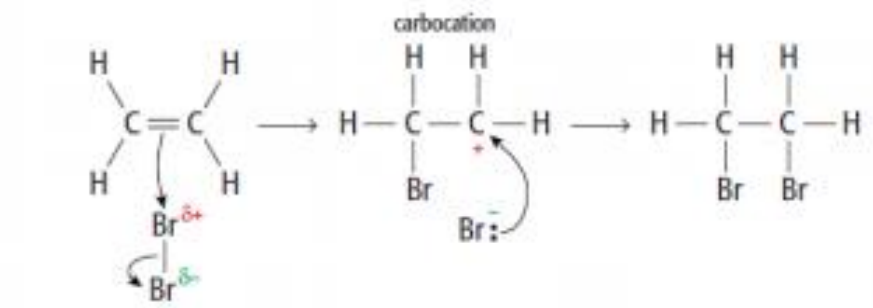
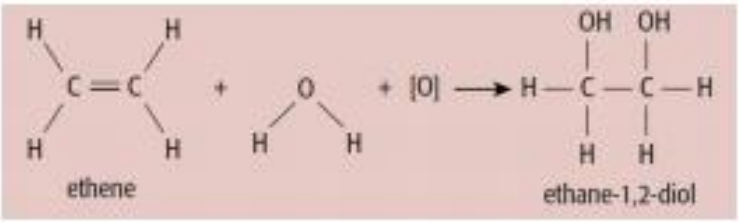


Figure 15.16 The mechanism of electrophilic addition of bromine to ethene.

- **Oxidation**:
  - Cold Dilute Acidified Manganate(VII) Solution ($KMnO_4$)



  - Hot Concentrated Acidified Manganate(VII) Solution ($KMnO_4$)

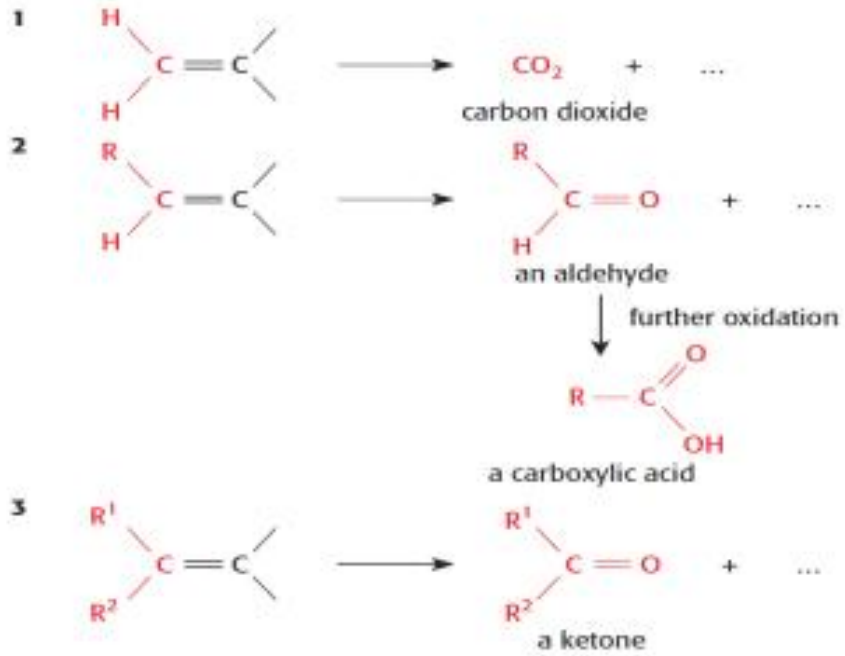


Figure 15.17 Oxidation with hot, concentrated manganate(VII) solution.

- Addition Polymerisation

eg: $CH_4 + Cl_2 \xrightarrow[\text{light}]{UV} CH_3Cl + HCl$

initiation: $Cl_2 \xrightarrow[\text{light}]{UV} 2\,Cl\cdot$ (homolytic fission)

propagation: $CH_4 + Cl\cdot \longrightarrow \cdot CH_3 + HCl$

$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$

termination: $\cdot Cl + \cdot CH_3 \longrightarrow CH_3Cl$

$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$