HYDROCARBONS - ALKANES AND CYCLOALKANES TUTORIAL

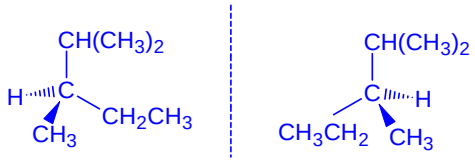
Suggested answers

Structure and naming

1 Give the IUPAC name for each compound. Identify any chiral center and draw its stereoisomers, if any.

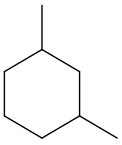
(a) $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$ 4-methylheptane; no chiral C

(b) $CH_3CH(CH_3)CH(CH_3)CH_2CH_3$ 2,3-dimethylpentane



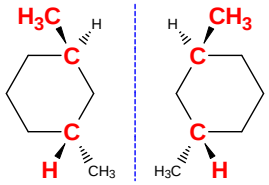
enantiomers

(c)

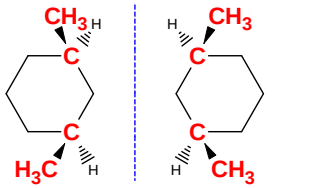


1,3-dimethylcyclohexane

(2 chiral centres with internal mirror plane; actual no of stereoisomers = 3)



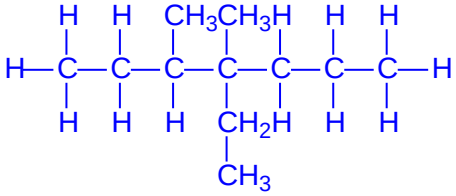
non-superimposable mirror images;



superimposable mirror images
(identical structures)

2 Give the structural formula of the following alkanes.

(a) 4-ethyl-3,4-dimethylheptane



(b) a saturated compound with molecular formula C_5H_{10}

(cannot be alkene; must be cycloalkane - any of the structures below)

Physical Properties

3 Crude oil consists mainly of alkanes, the saturated hydrocarbons. The alkanes in crude oil can be separated because they have different boiling points.

The table below shows the boiling points of some alkanes.

Alkane	Boiling point / ºC	M_r
Butane	0	58
Pentane	36	72
Hexane	69	86
2-methylbutane	28	72
2,2-dimethylpropane	10	72
3-methylpentane	?	86
2,3-dimethylbutane	58	86

(a) State what is meant by the term *saturated hydrocarbon*.

A compound containing:

- only C and H atoms where all C atoms form 4 single covalent bonds each.
- only single bonds, no multiple bonds

(b) **(i)** Explain the trend in boiling points of the straight chain alkanes.

boiling point increases from butane to hexane, due to:

- increasing M_r; hence size of electron cloud increases
- increasing electron cloud size leads to more easily induced dipole/ greater ease of distortion
- strength of intermolecular id-id interactions increases,
- bp increases as more E is required to break the increasingly stronger IMF

(ii) Explain the difference in the boiling points of the three isomers with $M_r = 72$.

- decreasing order of bp: pentane > 2-methylbutane > 2,2-dimethylpropane
- increasing branching of isomers leads to smaller surface area of contact between molecules
- hence weaker intermolecular id-id interactions
- less E needed to break the IMF and hence decreasing bp in branched compounds

(iii) With reference to your answer in **b(ii)**, suggest a possible value for the boiling point of 3-methylpentane.

Any value: 58 ºC - 69 ºC (higher than 2,3-dimethylbutane but lower than hexane)

Combustion of hydrocarbon

4 What is the volume of CO_2 formed when y cm^3 of a 50:50 mixture of methane and propane is completely burnt?

A 2y cm^3 **B** $\frac{5y}{2}$ cm^3 **C** 4y cm^3 **D** 5y cm^3

	$CH_4 + 2O_2 \rightarrow$	$CO_2 + 2H_2O$
V / cm^3	½y	½y

	$C_3H_8 + 5O_2 \rightarrow$	$3CO_2 + 4H_2O$
V / cm^3	½y	$\frac{3y}{2}$

Total vol of CO_2 produced = 2y cm^3 **Ans: A**

5 When 15 cm^3 of a gaseous hydrocarbon **A** were burned in 100 cm^3 of oxygen, the final gaseous mixture contained 60 cm^3 of carbon dioxide and 10 cm^3 of unreacted oxygen. [All gaseous volumes measured under identical conditions.]

What is the formula of hydrocarbon **A**?

A C_3H_6 **B** C_3H_8 **C** C_4H_8 **D** C_4H_{10}

Let **X** be C_xH_y

	$C_xH_y + (x + \frac{y}{4})O_2 \rightarrow$		$xCO_2 + \frac{y}{2}H_2O$	
$V_{initial}$ / cm^3	**15**	**100**	**0**	**-**
V_{final} / cm^3	**0**	**10**	**60**	**-**
Reacting vol	**15**	**90**	**60**	**-**
Vol ratio	**1**	**6**	**4**	

By Avagadro's law: V ∝ n at constant p and T

x = 4; $x + \frac{y}{4} = 6$, y = 8

Ans: C

6 (2016 P3 Q1c) Carbon monoxide is a product of the incomplete combustion of hydrocarbons in internal combustion engines.
Write an equation for the incomplete combustion of octane, C_8H_{18}, giving CO_2 and CO in a 3:1 molar ratio.

$C_8H_{18} + \frac{23}{2} O_2 \rightarrow 6CO_2 + 2CO + 9H_2O$

Free Radical Substitution

7 (2016 P3 Q4d) Alkanes are very unreactive.

(i) Suggest two reasons why this is the case.

(ii) However, alkanes such as propane, C_3H_8, do react with oxygen and with chlorine.
For each of these reactions,

- State the conditions under which the reaction is carried out.
- Name the *type of reaction* which takes place,
- Write an equation for the reaction.

(i)
The C−C (BE = 350 kJ mol^{-1}) and C−H bonds (BE = 410 kJ mol^{-1}) are strong.
Larger amount of energy is required for reaction to occur.
The C−C and C−H bonds are non polar, thus they do not attract electrophiles and nucleophiles.
(ii)
$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
Conditions: Burn propane in excess O_2
Type of reaction: Combustion

$C_3H_8 + Cl_2 \rightarrow CH_3CH_2CH_2Cl + HCl$
Conditions: Cl_2(g), UV light
Type of reaction: Free radical substitution
Note: Mechanism for free radical substitution is not required.

8 Which explains why chlorine gas reacts readily with ethane in the presence of ultraviolet light?

A UV light breaks the C-H bonds in ethane.

B UV light increases the temperature of the mixture.

C UV light splits the chlorine molecules into chlorine atoms.

Note: In initiation step, homolytic fission of chlorine molecules into chlorine radicals (which is chlorine atoms) take place in presence of UV light.

D UV light breaks up the chlorine molecules into chloride ions.

Ans: C

9 Which statement best explains why a high yield of 2-bromobutane is **not** usually obtained when butane and bromine react in the presence of UV light?

A Bromine reacts with butane too vigorously.

B Bromine can replace any hydrogen atom in butane.

When monobromination take place in presence of limiting Br_2, 1-bromobutane and 2-bromobutane can be formed. Also, poly-substitution can also take place if excess Br_2 is used.

C The second and third carbon atoms of butane are too strongly electrophilic.

D The second and third carbon atoms of butane are too strongly nucleophilic.

Ans: B

10 Which is a **propagation** step in the reaction between propane and bromine when they are irradiated with ultraviolet light?

A $CH_3CH_2CH_2Br + Br\bullet \rightarrow CH_3CH_2\dot{C}H_2 + Br_2$

B $CH_3CH_2\dot{C}H_2 + Br\bullet \rightarrow CH_3CH_2CH_2Br$

C $CH_3CH_2\dot{C}HBr + Br_2 \rightarrow CH_3CH_2CHBr_2 + Br\bullet$

D $CH_3CH_2\dot{C}H_2 + Br_2 \rightarrow CH_3CH_2CHBr + HBr$

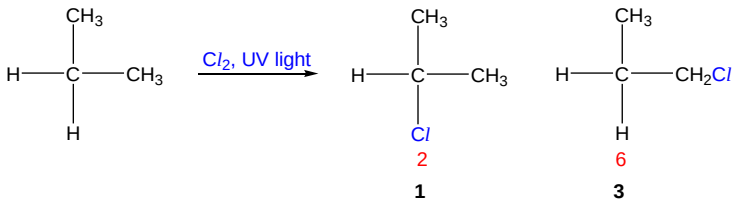
Every propagation step should involve consumption of one radical & production of another radical. Option D is incorrect.
Option B is Termination step between 2 radicals.
Option A should generate an organic radical and HBr. It is not energetically favorable to break C—Br bond (280 kJ mol^{-1}) and form a weaker Br—Br bond (193 kJ mol^{-1}).

Ans: C

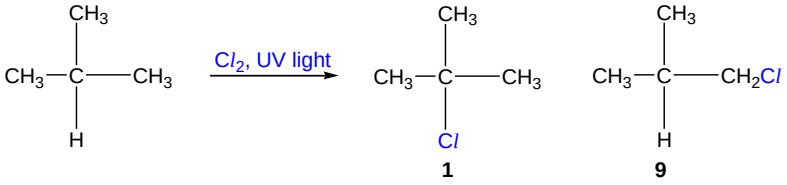
11 An alkane **J** is reacted with chlorine gas in the presence of ultraviolet light to form only two monochlorinated alkanes in an approximate molar ratio of 6 : 1.

Which could be **J**?

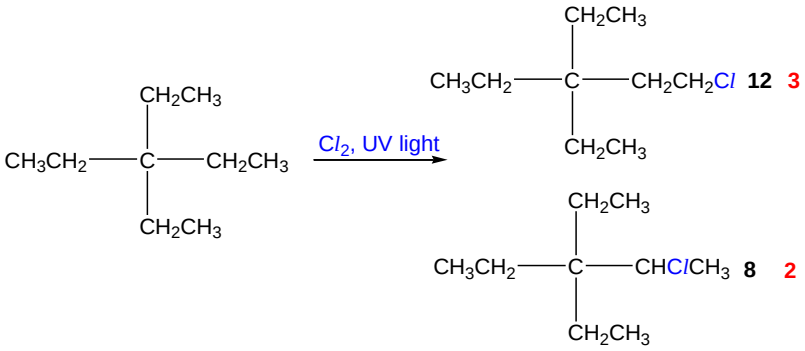
A



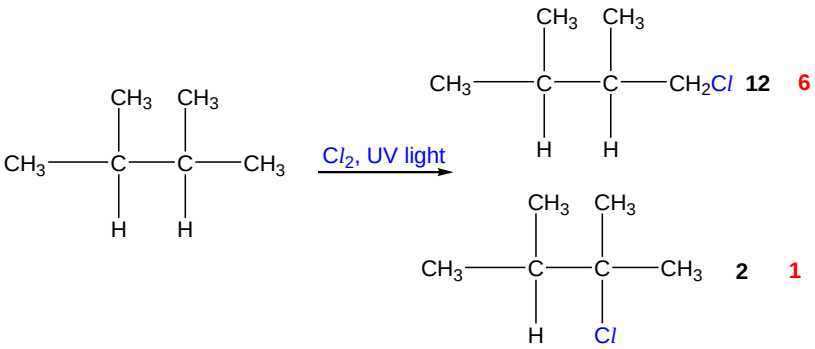
B



C



D



Ans: D

12 Propane reacts with chlorine gas in the presence of UV light.

Which is true about the reaction?

A The maximum number of mono-chlorinated structural isomers with formula C_3H_7Cl is 2.

True. 1-chloropropane and 2-chloropropane

B C_6H_{12} is present in a small quantity in the product.

False. The radical formed in propagation is C_3H_7 radical

Termination involving two C_3H_7 radical gives C_6H_{14}.

C Homolytic fission occurs only in the initiation step.

False. Homolytic fission also occur in propagation steps.

Propagation steps involve homolytic fission that generate free radical.

D HCl is formed in the termination step.

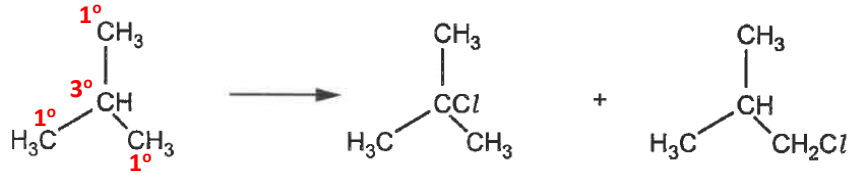
False. HCl is only formed in propagation step.

Ans: A

13. It is found by experiment that during free radical substitution, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

reaction	relative rate
$RCH_3 \longrightarrow RCH_2Cl$	1
$R_2CH_2 \longrightarrow R_2CHCl$	7
$R_3CH \longrightarrow R_3CCl$	21

Predict the relative ratio of the two possible products L and M from the chlorination of 2-methylpropane, using the information in the table above, together with the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule.
Explain your answer.



2-methylpropane L M

No. of H atoms that can be substituted to give this product	1 (tertiary hydrogen atom)	9 (primary hydrogen atom)
Relative rate	21 (tertiary hydrogen atom)	1 (primary hydrogen atom)
Yield	$1 \times 21 = 21$	$9 \times 1 = 9$
Relative ratio	7	3

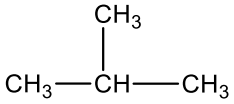
14 **A** and **B** are two structural isomers with the molecular formula C_4H_{10}.

When **A** reacts with chlorine gas in the presence of light, two monochlorinated alkanes **C** and **D** are formed. Only **D** contains a chiral carbon.

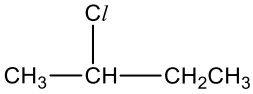
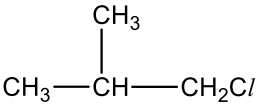
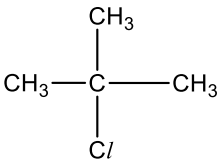
When **B** reacts with chlorine gas in the presence of light, two monochlorinated alkanes **E** and **F** are formed.

Identify **A**, **B**, **C**, **D**, **E** and **F** by drawing their structural formulae.

(a) Possible structural isomers for C_4H_{10} are $CH_3CH_2CH_2CH_3$ and $CH_3CH(CH_3)_2$

A $CH_3CH_2CH_2CH_3$ **B** 

C $CH_3CH_2CH_2CH_2Cl$

D  **E and F**  

(b)(i) A and B are chain isomers

(ii) C and D are positional isomers

15 In an experiment, propane is added to liquid bromine in the dark. When the reaction mixture is exposed to sunlight, the reddish brown colour slowly disappears and a misty gas is given off.

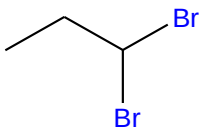
(i) Identify the misty gas formed in the reaction.

The misty gas produced is HBr.

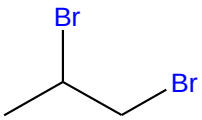
(ii) Write an overall equation for the reaction of one mole of propane, C_3H_8, with two moles of bromine.

Draw the structural formulae of all the possible products formed.

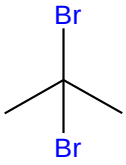
$CH_3CH_2CH_3 + 2Br_2 \rightarrow C_3H_6Br_2 + 2HBr$



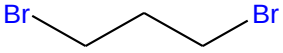
1,1-dibromopropane



1,2-dibromopropane



2,2-dibromopropane



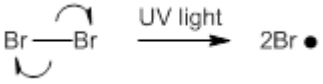
1,3-dibromopropane

(iii) Outline the mechanism for the formation of 1,2-dibromopropane in **b(ii)**.

There are four steps in the propagation stage of the mechanism.

Free radical substitution

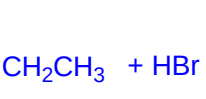
I **Initiation** (formation of reactive free radicals):

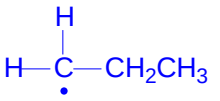
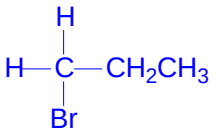


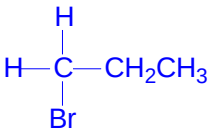
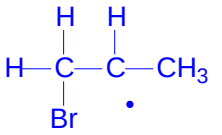
II **Propagation** (molecule + free radical → new molecule + new radical):

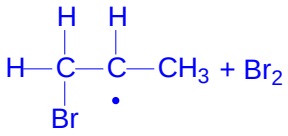
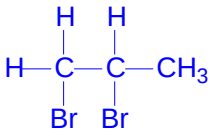
(a) C_1 lose H
(b) C_1 radical gain Br
(c) C_2 lose H
(d) C_2 radical gain Br

(Note: Sequence of C_1 or C_2 forming radical is interchangeable, e.g. C_2 forms radical first, C_1 forms radical later)

(a) $CH_3CH_2CH_3 + Br\bullet \longrightarrow$  $+ HBr$

(b)  $+ Br_2 \longrightarrow$  $+ Br\bullet$

(c)  $+ Br\bullet \longrightarrow$  $+ HBr$

(d)  $\longrightarrow$  $+ Br\bullet$

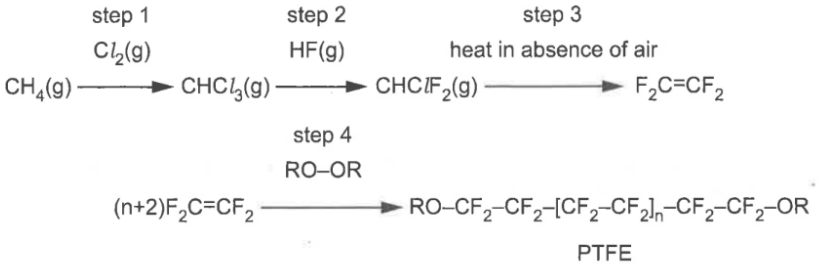
III **Termination** (reaction of 2 free radicals to form stable compounds): any 2 equations

$\bullet CH_2CH_2CH_3 + Br\bullet \rightarrow BrCH_2CH_2CH_3$

$2\bullet CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2CH_2CH_3$

$2Br\bullet \rightarrow Br_2$

16 (2021 P2 Q4d) The term 'polymer' is given to a large molecule made up of many repeat units. Poly(tetrafluoroethane), PTFE, is a polymer made from many tetrafluorethane molecules, $F_2C{=}CF_2$. PTFE can be manufactured from methane in a series of steps.



Step 4 occurs via four separate reactions, **A** to **D**.

A Homolytic fission of RO−OR at 330K and 10-20 atm to produce two RO• radicals

B RO• reacts with one $F_2C{=}CF_2$ molecule to produce a new radical

C Repeated steps involving production of a series to produce

$$RO{-}CF_2{-}CF_2{-}[CF_2{-}CF_2]_n{-}CF_2{-}CF_2\bullet$$

D Two radicals combine to form $RO{-}CF_2{-}CF_2{-}[CF_2{-}CF_2]_{(2n+2)}{-}CF_2{-}CF_2{-}OR$

(i) Explain what is meant by the term homolytic fission.

it refers to an even breaking of a covalent bond where one electron from the bond goes to each of the atom, forming radicals.

(ii) Name reactions **A** to **D**.

A: Initiation
B: Propagation
C: Propagation
D: Termination

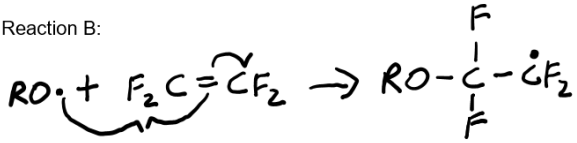
(iii) Suggest a name for the overall mechanism of step 4.

Free radical addition

(iv) Suggest the mechanism which occur in reactions **A** and **B** of step 4. Use curly arrows to show movements of electrons.

Reaction A:

Reaction B:



Petroleum and its environmental consequences

17 (2020 P1 Q20) Exhaust fumes from car engines contain the gases carbon dioxide, nitrogen oxides and unburnt hydrocarbons.

Use of a catalytic converter in the car exhaust changes the gases emitted.

Which statements are correct about the reactions occurring in the catalytic converter?

1. Carbon dioxide is removed by reduction.
2. Oxides of nitrogen are removed by reduction.
3. Unburnt hydrocarbons are removed by oxidation.

A 1 and 3 **B** 2 and 3 **C** 1 only **D** 2 only

Statement 1 is wrong: CO_2 is *produced* in the reactions in the catalytic converter.
Statement 2 is correct: $NO + CO \longrightarrow CO_2 + \frac{1}{2} N_2$.
Statement 3 is correct: Unburnt hydrocarbon undergoes oxidation to give $CO_2 + H_2O$.

18 Car exhausts contain a range of toxic substances that can have a serious impact on health. Once released into the air, these substances are breathed in and transported in the blood stream to all the body's major organs.

A typical composition of gases in petrol engine exhaust fumes is as follows.

Substance	**%**
Water vapour	9
Carbon dioxide	8
Carbon monoxide	4-6
Oxygen	4
Hydrocarbons	0.2
Oxides of nitrogen	0.3

(a) Which gases of exhaust fumes are consequences of incomplete combustion?

CO, hydrocarbons

(b) Suggest why the exhaust gases contain products of incomplete combustion.

any one:

- short reaction time in the car engine
- poor maintenance of the car engine
- limited oxygen supply in the combustion chamber

(c) Name a pollutant in the exhaust fumes that has an adverse effect on human health and explain its impact on human health.

CO. It binds irreversibly with haemoglobin in blood by forming a stable complex and reduces the capacity of haemoglobin to transport oxygen.

(d) Suggest one substance in the exhaust fumes which can convert one of the pollutants into harmless product in a car fitted with a catalytic converter. Write a chemical equation to support your suggestion.

NO.

$2NO + 2CO \rightarrow N_2 + 2CO_2$