

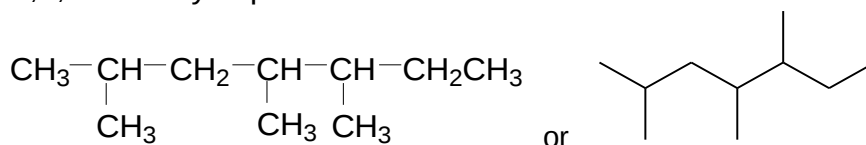


Tutorial 10: Hydrocarbons – Alkanes (Suggested Answers)

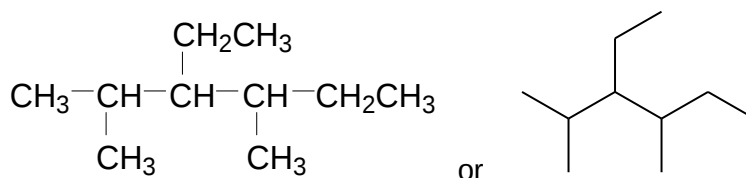
Self-Check Questions – Suggested Answers

- 1 (a) (i) 3,3-diethyl-4-methylheptane
(ii) 4-ethyl-2,2,3,6-tetramethyloctane
(iii) 3-ethyl-2,7-dimethyloctane
(iv) 2,2,5-trimethylheptane
(v) 3,3,4-triethylhexane

- (b) (i) 2,4,5-trimethylheptane



- (ii) 3-ethyl-2,4-dimethylhexane



- 2 The given compounds have simple molecular structures and can be arranged in the following order of increasing boiling point:

2-methylpentane < hexane < 3,3-dimethylpentane < 2-methylhexane < heptane

i.e. (e) < (d) < (c) < (a) < (b)

Comparing (c), (a) and (b) vs (e) and (d)

- (c), (a) and (b) are seven-carbon alkanes while (e) and (d) are six-carbon alkanes. (c), (a) and (b) have more electrons per molecule and hence, larger and more polarisable electron clouds than (e) and (d). Hence, the instantaneous dipole-induced dipole interactions in (c), (a) and (b) are stronger and more heat is required for boiling these alkanes, resulting in them having a higher boiling point than (e) and (d).

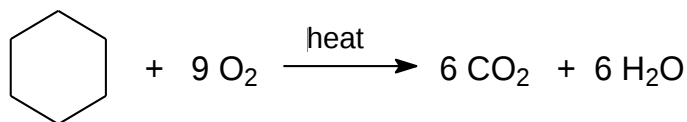
Comparing (c), (a) and (b)

- the degree of branching decreases from (c) to (a) to (b)
- there is increasing surface area of contact between molecules from (c) to (a) to (b)
- strength of instantaneous dipole-induced dipole interactions increases from (c) to (a) to (b)
- higher boiling point from (c) to (a) to (b)

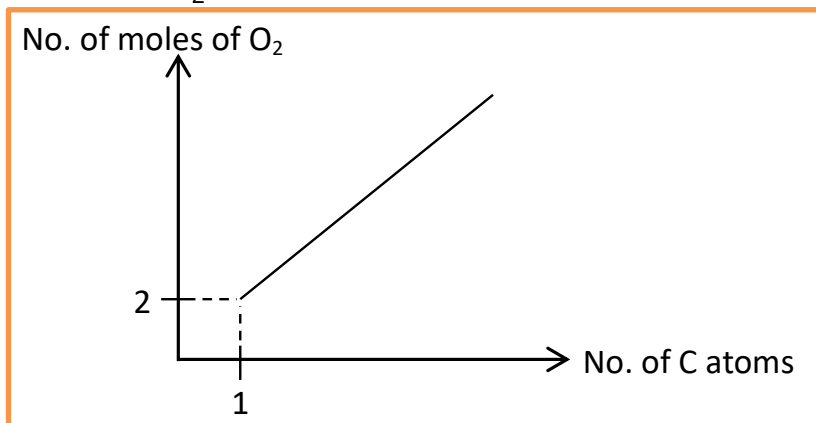
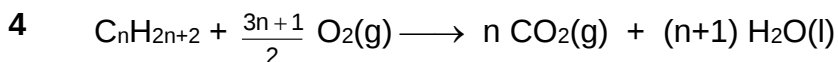
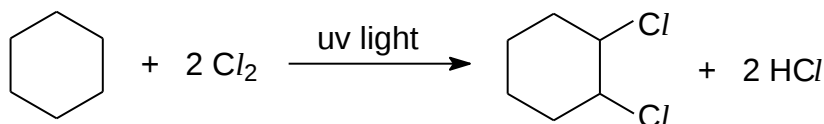
Comparing (e) and (d)

- the degree of branching decreases from (e) to (d),
- there is greater surface area of contact between molecules of (d),
- hence stronger instantaneous dipole-induced dipole interactions in (d)
- higher boiling point for (d)

3 Reaction (1): **Combustion**



Reaction (2): **Free-radical substitution**



- 5(a) Volume of unreacted O_2 and $\text{CO}_2 = 250 \text{ cm}^3$
 Volume of unreacted $\text{O}_2 = \text{volume of residual gas (after shaking with NaOH)} = 100 \text{ cm}^3$
 Volume of CO_2 produced = $250 - 100 = 150 \text{ cm}^3$

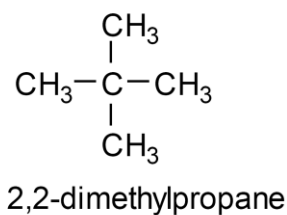
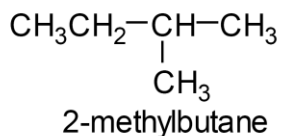
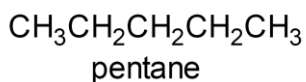
	$\text{C}_x\text{H}_y + (x + y/4)\text{O}_2(\text{g}) \rightarrow x\text{CO}_2(\text{g}) + y/2 \text{H}_2\text{O}(\text{l})$			
volume used/ cm^3	30	340	-	-
volume reacted/ cm^3	30	$(340 - 100) = 240$	$(250 - 100) = 150$	
volume ratio	1	: 8	: 5	
molar ratio	1	: 8	: 5	
molar ratio	1	: $(x + y/4)$	: x	

From the table, **x = 5**

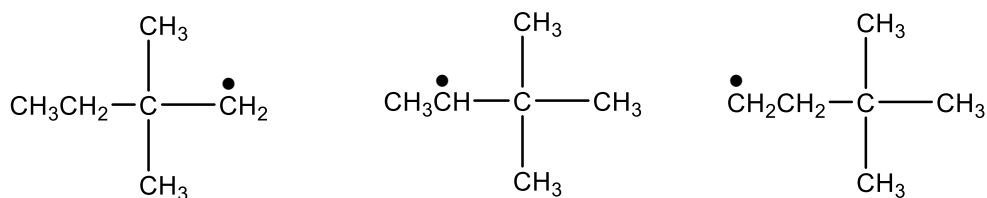
And $(x + y/4) = 8 \Rightarrow \mathbf{y = 12}$

Hence, the molecular formula of the hydrocarbon is **C₅H₁₂**.

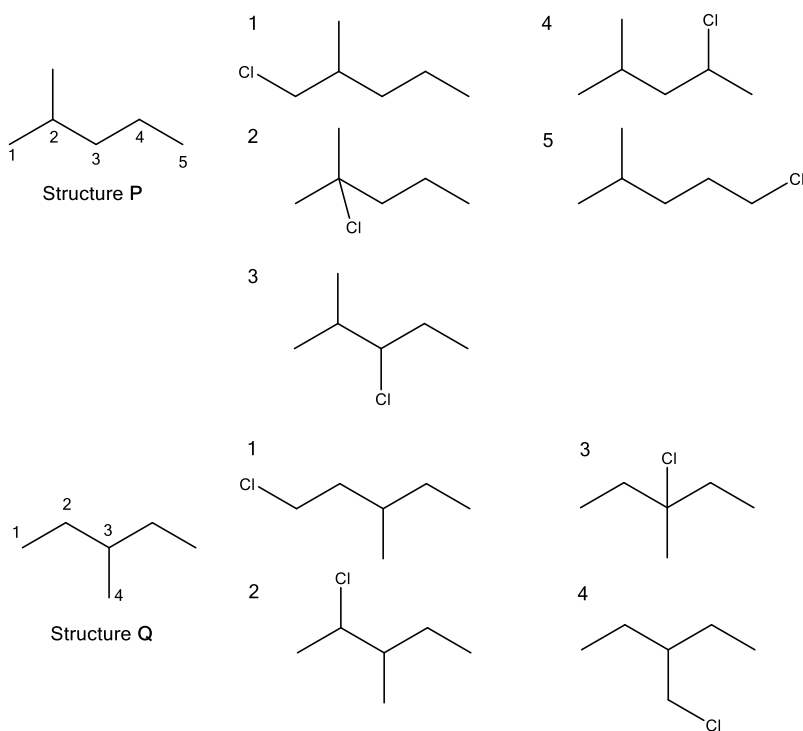
- 5(b) • Possible isomers of the alkane:



- 6 Answer : C
Possible answers:



- 7 Answer : B

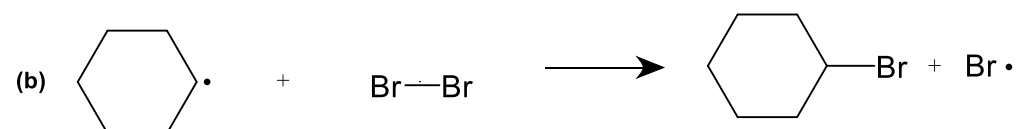


- 8 The mechanism is **free-radical substitution** which consists of the following steps:

Step 1: Initiation

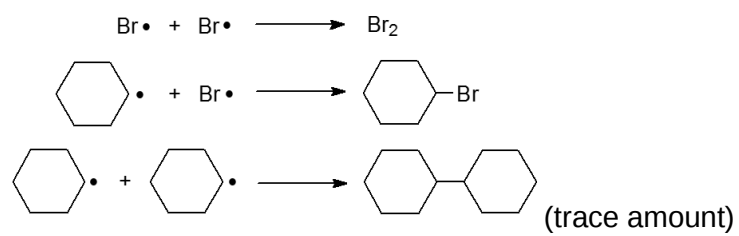


Step 2: Propagation



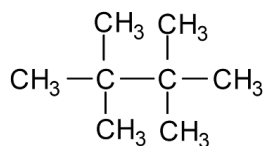
Then (a), (b), (a), (b),

Step 3: Termination

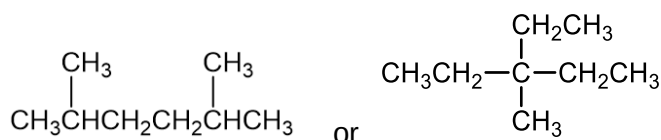


Practice Questions – Suggested Answers

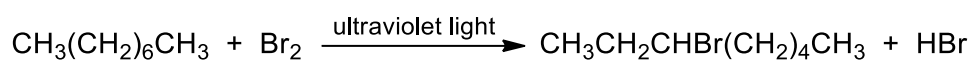
9(a)(i)



9(a)(ii)



9(b)(i)



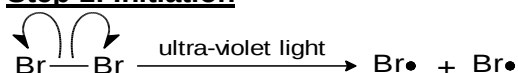
9(b)(ii)

Orange-red bromine is decolourised and **white fumes of HBr** which turn damp blue litmus paper red are formed.

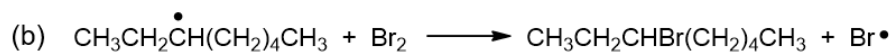
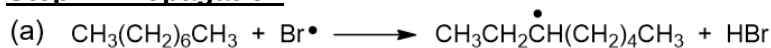
9(b)(iii)

The mechanism is **free-radical substitution**

Step 1: Initiation

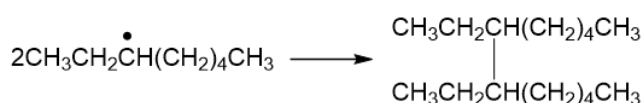
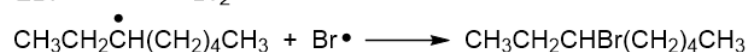


Step 2: Propagation



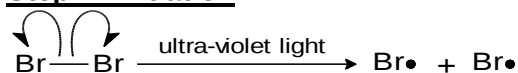
Then (a), (b), ...

Step 3: Termination

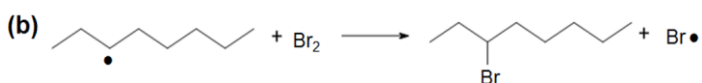


Note: Skeletal formulae may be used.

Step 1: Initiation

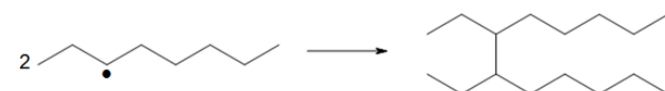
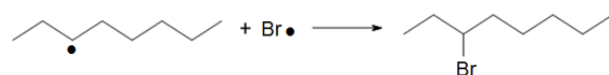


Step 2: Propagation



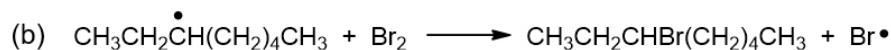
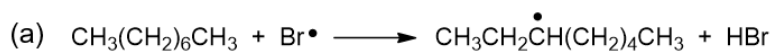
Then (a), (b), ...

Step 3: Termination



9(b)(iv) A flash of ultraviolet light provides enough energy for some Br₂ molecules to undergo homolytic bond fission to form Br• radicals. Once the Br• radicals are generated in the initiation step, the chain reaction is started and the propagation steps can proceed successively for many cycles un-aided.

9(b)(v) Consider the 2 propagation steps:

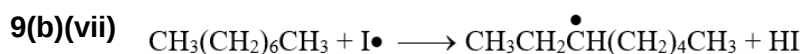


Then (a), (b), ...

The reaction is an example of homogeneous catalysis since the catalyst, Br•

- exists in the same phase (dissolved in inert solvent) as the two reactants, octane and Br₂.
- is consumed in one step and regenerated in another.

9(b)(vi) Use an excess of octane (or use a limiting amount of Br₂).



ΔH reaction for the 1st propagation step = BE(C–H) – BE(H–I) = +410 – 299 = **+111 kJ mol⁻¹**

The first propagation step is **endothermic** due to the breaking of the relatively strong C–H bond and the formation of the weaker H–I bond. This makes it difficult for the chain propagation steps to occur. Thus, the formation of 3-iodooctane is energetically unfavourable.

10(a)

$$\text{Molar ratio of C to H in alkane F} = \frac{83.72}{12.0} : \frac{(100-83.72)}{1.0} = 6.977 : 16.28 = 1 : 2.33 = 3 : 7$$

Hence, the **empirical formula of F** is **C₃H₇**.

Let the molecular formula of **F** be (C₃H₇)_m, i.e. C_{3m}H_{7m}.

The general formula of an alkane is C_nH_{2n+2}.

In this case, 3m = n

$$\text{and } 7m = 2n + 2$$

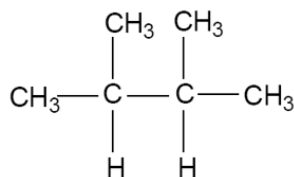
Upon solving the simultaneous equations, m = 2

Hence, the **molecular formula of F** is **C₆H₁₄**.

F undergoes **free-radical substitution** reaction with Br₂ to form only two mono-brominated products.

⇒ There are **2 types of H atoms** in a molecule of **F**.

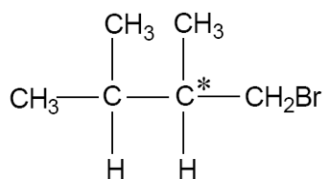
⇒ **F** has to be



H is a mono-brominated product and is chiral.

⇒ **H** contains **a chiral carbon** atom.

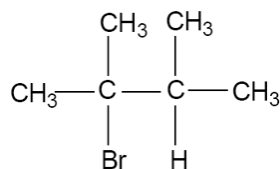
⇒ **H** is



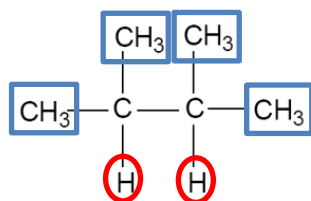
Note: * denotes a chiral carbon atom

G is the other mono-brominated product.

⇒ **G** is



10(b)



To form **G** from **F**, the Br atom can replace any one of the **2 tertiary hydrogen atoms** (denoted by the circle).

To form **H** from **F**, the Br atom can replace any one of the **12 primary hydrogen atoms** (denoted by the box).

Hence, based on probability factor (and assuming all the hydrogen atoms have the same reactivity), the approximate molar ratio in which **G** and **H** are formed = 2 : 12 = **1 : 6**

Note #1:

- Can proceed by trial and error to find m.
- In this case, m ≠ 1 and m ≠ 3
- When m = 2, the molecular formula is C₆H₁₄ which fits that of a six-carbon alkane.

Note #2:

- Let **F** have n carbon atoms and have the general alkane formula, C_nH_{2n+2}.
- Then % of carbon (by mass) in **F** = $\left(\frac{12n}{14n+2} \times 100\right) = 83.72$
Hence n = 6.06 = 6

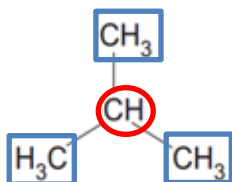
Note #3:

- **F** is not a cycloalkane since percentage of carbon by mass in a cycloalkane is not 83.72%.

11(a) These reagents do not attack an alkane because

1. Alkanes are non polar.
 - They do not contain any region of high electron density and thus do not attract electrophilic reagents.
 - They also do not contain any electron-deficient sites to attract nucleophilic reagents.
2. Alkanes have relatively strong C–C and C–H bonds which do not break under normal conditions.

11(b)



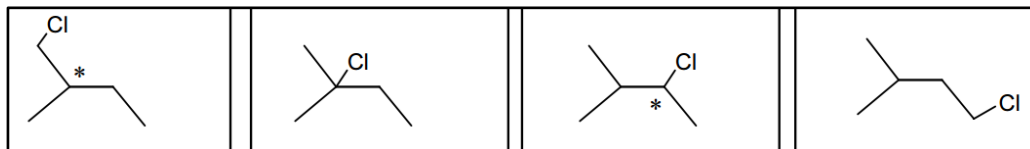
To form **A**, the Cl atom can replace the only 1 tertiary H atom (denoted by the circle) in 2-methylpropane.

To form **B**, the Cl atom can replace any one of the 9 primary H atoms (denoted by the box) in 2-methylpropane.

Note: In this example, substituting any primary H in 2-methylpropane results in the same product. This is only true because in this case, the primary H atoms are all equivalent.

Combining both the probability factor stated above and the given reactivity ratio factor, the relative ratio of **A** to **B** = (1)(21) : (9)(1) = 21:9 = **7:3**

11(c)



Total number of isomers: 6

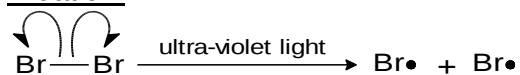
12(a)(i) Secondary free radical is more stable than primary free radical. **[1]**

12(a)(ii) The free radical has a C atom with an unpaired electron/is electron deficient. Since a secondary free radical has 2 electron donating alkyl groups directly attached to this C atom compared to only one in a primary free radical, the secondary radical is more stable. **[1]**

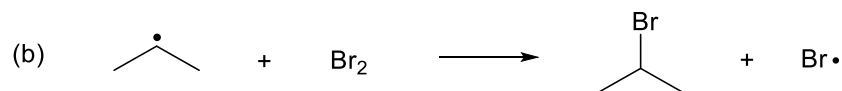
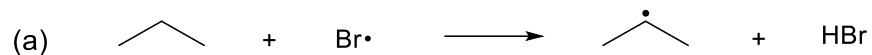
12(a)(iii) Homolytic fission of the C–H bond in $(\text{CH}_3)_2\text{CH-H}$ results in the formation of a more stable secondary free radical, $(\text{CH}_3)_2\dot{\text{C}}\text{H}$. **[1]**

12(b) Free radical substitution

Initiation:



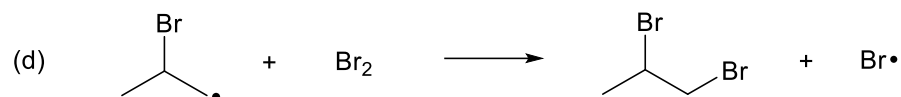
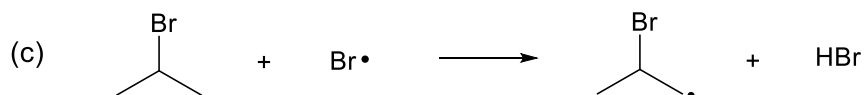
Propagation:



Then (a), (b), (a), (b), ...

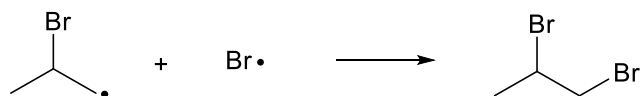
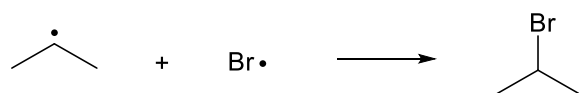
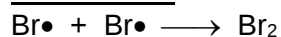
Propagation steps (a) and (b) give rise to many molecules of $\text{CH}_3\text{CHBrCH}_3$.

$\text{CH}_3\text{CHBrCH}_3$ can undergo further bromination via propagation steps (c) and (d) to form $\text{CH}_3\text{CHBrCH}_2\text{Br}$.



Then (c), (d), (c), (d), ...

Termination:



Note: 1-bromopropane can also be formed first followed by 1,2-dibromopropane.