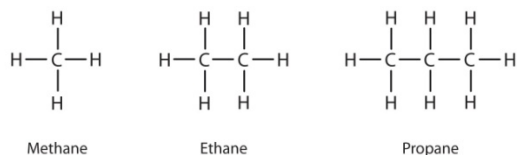


ALKANES

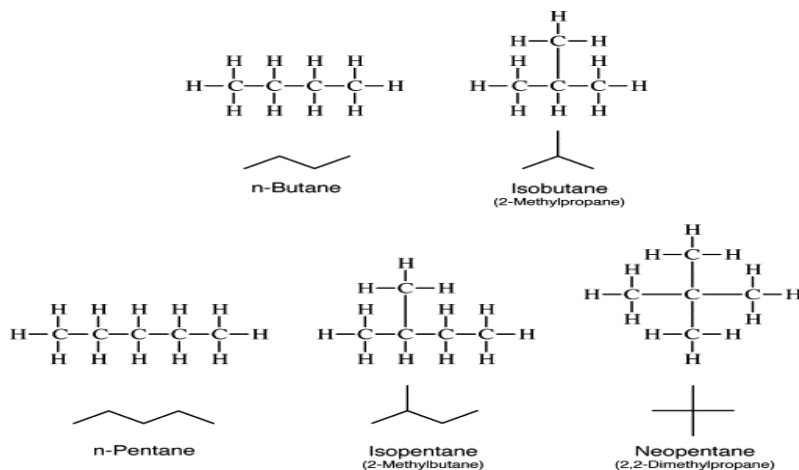
Kumud Bala

Saturated hydrocarbon can be either acyclic or cyclic. The acyclic saturated hydrocarbons are called paraffins (Latin: Parum= little, affinis = affinity) since they are relatively unreactive towards most of the reagents such as acids, bases, oxidizing and reducing agent. However, under drastic conditions, i.e., at high temperature and pressure, alkanes do undergo different types of reactions like halogenation, nitration, sulphonation, pyrolysis, etc.

Isomerism of alkanes: Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers. The phenomenon of existence of two or more compounds for possessing the same molecular formula but different properties is called isomerism. The alkanes show structural isomerism in which the isomers differ in the skeleton or chain of carbon atoms. For example, first three members of the alkane family do not exhibit chain isomerism because they have only one structure formula. Methane, ethane, propane has only one structure since there is only one way in which one, two and three carbon atoms can be connected.

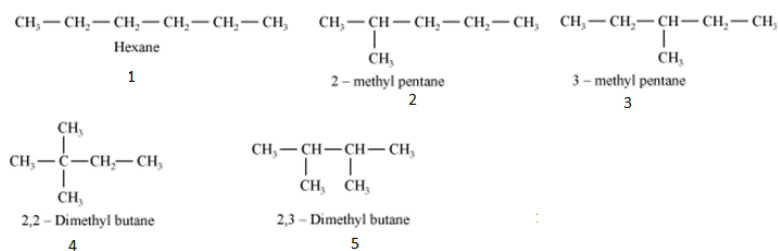


For butane two isomers are possible since four carbon atoms can be joined in two different ways.



Now five carbon atoms in pentane can be joined in three different ways and hence pentane has three isomers.

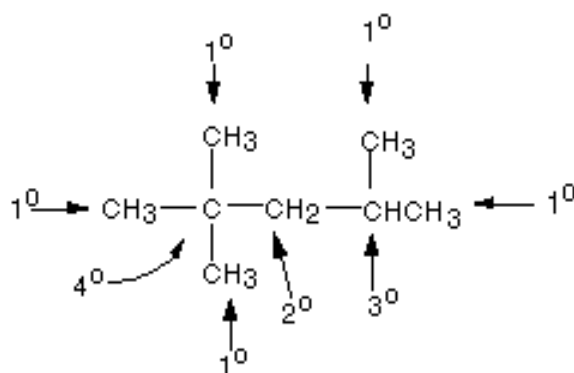
Six carbon atoms in hexane can be arranged in five different ways. Thus, hexane has five isomers. These are:



Similarly, we can show that heptane (C₇H₁₆) has 9, octane (C₈H₁₈) has 18, nonane (C₉H₂₀) has 35 while decane (C₁₀H₂₂) has 75 isomers. Such structure isomers which differ in the arrangement of carbon chain are called chain or nuclear isomers.

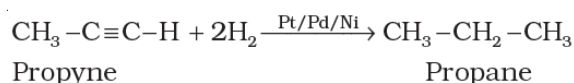
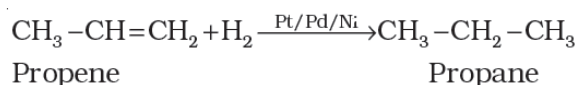
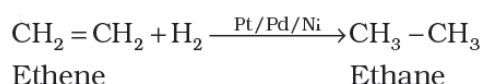
Type of carbon and hydrogen atoms in alkanes: The carbon atoms in an alkane molecule may be classified into four types as primary (1°), secondary (2°), tertiary (3°) and quaternary (4°).

- (i) A carbon atom attached to one other or (no other) carbon is called primary carbon.
- (ii) A carbon atom attached to two other carbon atoms is called secondary carbon.
- (iii) A carbon atom attached to three other carbon atoms is called tertiary carbon.
- (iv) A carbon atom attached to four other carbon atoms is called quaternary carbon. Hydrogen atoms attached to Primary, secondary and tertiary carbon atoms are referred to as Primary, secondary and tertiary hydrogen atoms are respectively.

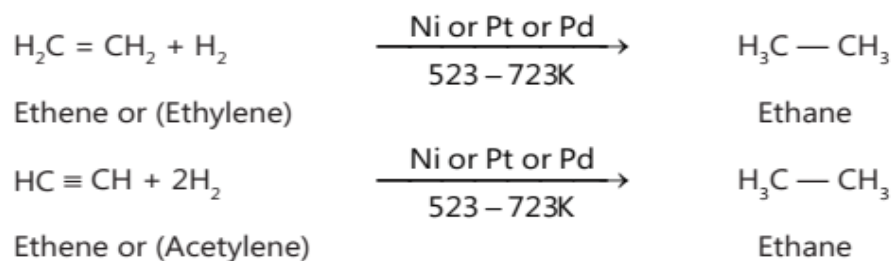


Methods of preparation of alkanes: Some of the laboratory methods of preparation of alkanes are following.

1. From unsaturated hydrocarbon: The process of addition of hydrogen to an unsaturated compound in the presence of a catalyst is called hydrogenation reaction. Alkenes and alkynes add one and two molecules of hydrogen respectively in the presence of a catalyst such as raney nickel, platinum or palladium to form alkane at ordinary temperature and pressure.



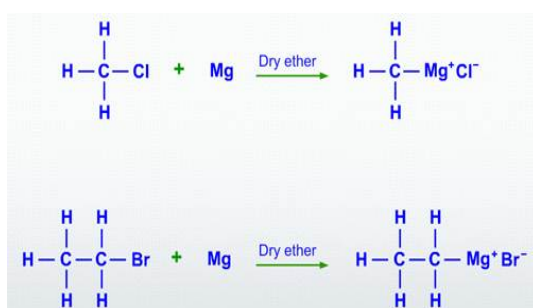
The hydrogenation of unsaturated hydrocarbon using ordinary nickel at a temperature of about 523-573K is commonly known as Sabatier and Sendern's reaction or reduction.



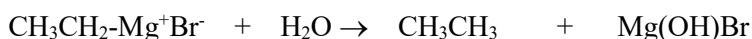
This hydrogenation reaction is used in the manufacture of Vanaspati Ghee from edible vegetable oils.

2. From alkyl halides: Alkyl halides can be converted into alkanes by any one of the following methods:

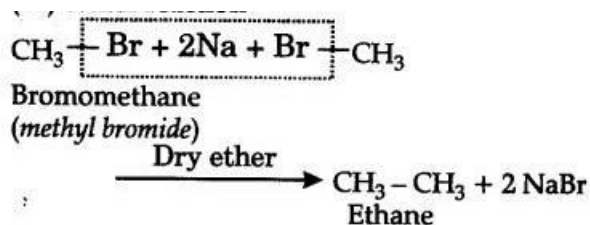
(i) through Grignard reagents: alkyl halides (bromides and iodides) react with magnesium metal in presence of dry ether to form alkyl magnesium halides. These are commonly known as Grignard reagents.



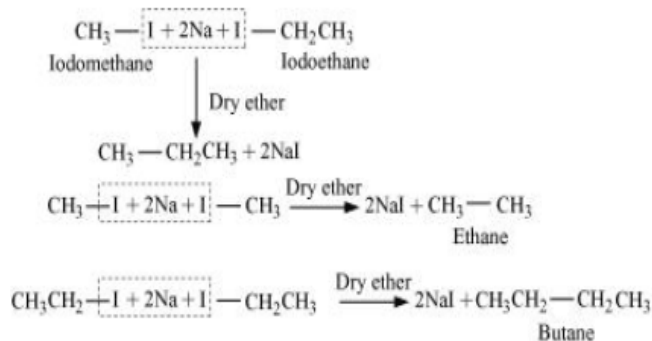
Since carbon is more electronegative (electronegativity = 2.5) than magnesium (electronegativity = 1.2) therefore, C-Mg bond is quite polar. Hence, Grignard reagents readily react with compound containing active hydrogen such as water, acids, alcohol, ammonia, amine etc. to form alkane. For example:



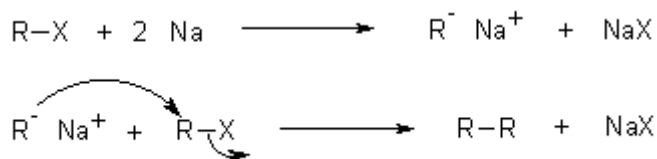
(ii) Wurtz reaction: when an alkyl halide is treated with metallic sodium in presence of dry diethyl ether, a symmetrical alkane, containing double the number of carbon atoms present in the alkyl group, is formed. This reaction is called Wurtz reaction.



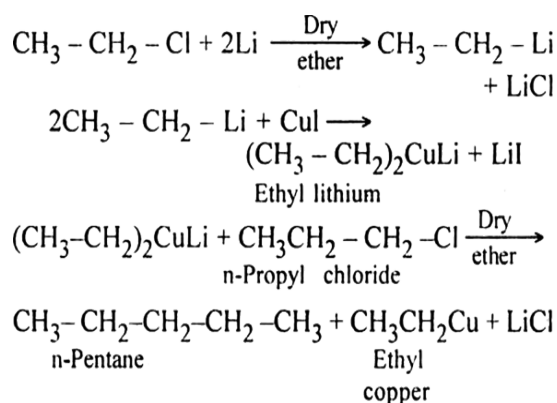
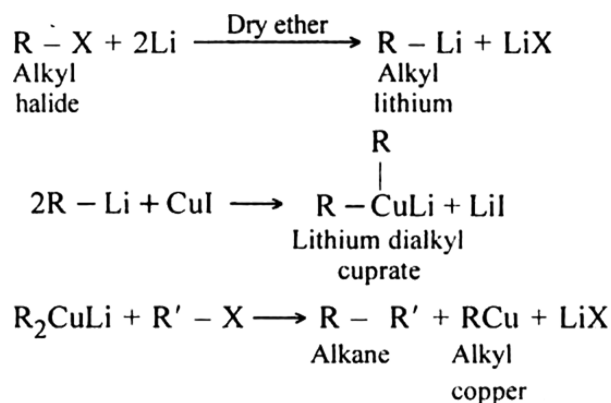
Thus, Wurtz reaction is a convenient method for the preparation of symmetrical alkane (R-R), i.e., alkane containing an even number of carbon atoms. However, if two different alkyl halides are used to prepare an alkane with odd number of carbon atoms, a mixture of three alkanes is actually produced. This is due to the reason that the two alkyl halides, in addition to reacting with each other, also react amongst themselves giving a mixture of three alkanes.



The boiling points of these alkanes are very close and hence they cannot be separated by fractional distillation. It is because of this drawback that Wurtz reaction is used for the synthesis of only symmetrical alkane and not for the preparation of unsymmetrical alkanes i.e., alkanes containing odd number of carbon atoms.

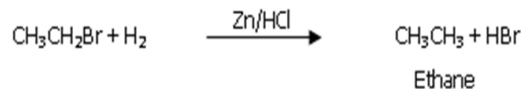
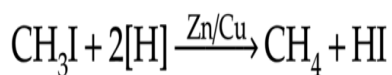


(iii) Corey-House reaction: Wurtz reaction does not give good yields of unsymmetrical contains alkanes, i.e., containing odd number of carbon atoms. However, Corey- House Reaction can be used to prepare both symmetrical and unsymmetrical alkanes in good yields. In this reaction the alkyl halide is first treated with lithium metal in dry ether to form alkyl lithium which is then allowed to react with cuprous iodide to yield lithium dialkyl copper. Lithium dialkyl copper thus obtained on subsequent treatment with suitable alkyl halide gives the desired alkane.



(iv) Reduction of alkyl halides:

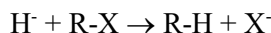
(a) Reduction by dissolving metals such as Zn and CH_3COOH or HCl, Zn and NaOH or Zn-Cu couple and alcohol.



However, with Zn/NaOH reduction occurs with nascent hydrogen.



(b) Reduction by chemically reagents such as LiAlH_4 , NaBH_4 and Ph_3SnH .

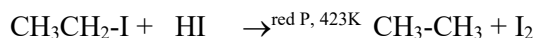
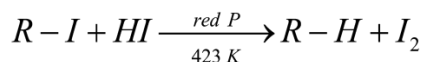


1° and 2° alkyl halides are readily reduced to alkane by lithium aluminium hydride (LiAlH_4) but 3° alkyl halides mainly undergo dehydrohalogenation to form alkenes. On the other hand, sodium boron hydride (NaBH_4) reduces 2° and 3° alkyl halides but not 1° whereas triphenyltin hydride reduces all the three types of alkyl halides.

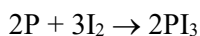
(c) Catalytic hydrogenolysis implies cleavage of a sigma bond with hydrogen in the presence of a catalyst. The best catalyst is platinum-carbon (Pd-C) but Raney Ni has also been effective provided if it is used in large excess.



(d) Reduction with HI and red P: alkyl iodides are readily reduced to the corresponding alkanes by heating with concentrated hydrogen iodide in presence of red phosphorus at 423K.



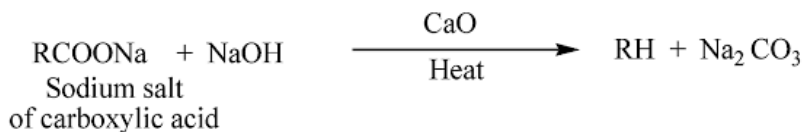
The purpose of red phosphorus is to remove the iodine liberated in the reaction, otherwise it would react with alkane to give back the alkyl iodide. It may be noted here that the alkane formed by this method has the same number of carbon atoms as the alkyl halide.

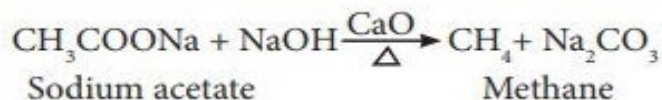


3. From carboxylic acids: alkanes can be prepared from carboxylic acid by the following two methods:

(i) Decarboxylation and (ii) Kolbe's electrolytic method

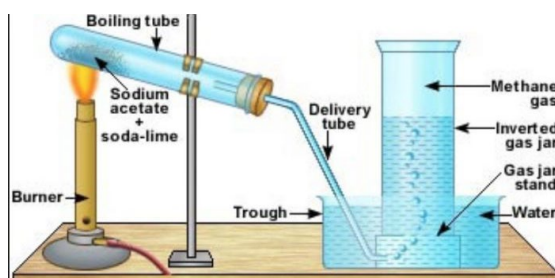
(i) **Decarboxylation:** the process of removal of a molecule of carbon dioxide from an organic compound is called decarboxylation. When a carboxylic acid is heated with soda lime ($\text{NaOH} + \text{CaO}$ in the ratio 3:1) at about 630K, a molecule of carbon dioxide is lost and an alkane with one carbon atom less than the carboxylic acid is formed.





Sodium Hydroxide alone could have been used in the above reaction but soda lime is preferred because of the following two reasons:

- Calcium oxide permits the reaction to be carried out at a relatively higher temperature to ensure complete decarboxylation.
- Calcium oxide keeps sodium hydroxide dry because it is quite hygroscopic (absorbs moisture from air) in nature. In the laboratory, methane is prepared by heating a mixture of sodium acetate and soda lime (in the ratio of 1:4) in a copper tube and the methane produced is collected by the downward displacement of water.



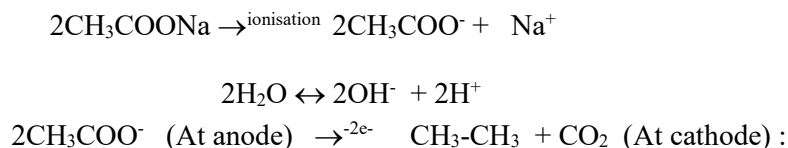
(ii) Kolb's electrolytic method: when a concentrated aqueous solution of the sodium or potassium salt of monocarboxylic acid is electrolysed, an alkane is produced.



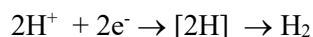
Thus, if n is the number of carbon atoms in the salt of the carboxylic acid, the alkane formed has $2(n-1)$ carbon atoms. Alternatively, if n is the number of carbon atoms in the alkyl group, the alkane formed has $2n$ carbon atoms. For example:



This reaction is believed to occur through the following steps:



Since the electrode potential of H^+ ions is higher than that of Na^+ ions, therefore, H^+ ions are preferentially discharged to produce H_2 while Na^+ ions remain in the solution.



Kolbe's reaction laid the foundation for the development of organo-electrochemistry.

Limitation: like Wurtz reaction, this is also used to prepare only alkanes with even number of carbon atoms and not alkanes with odd number of carbon atoms.

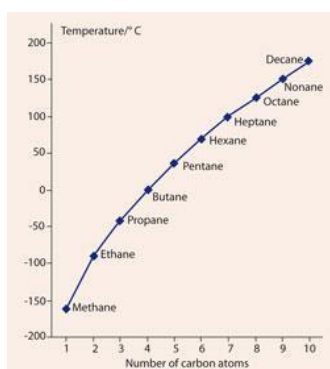
4. By the action of water on beryllium and aluminium carbide:






Physical properties of alkanes: The physical properties of the alkane depend upon the intermolecular force of attraction. Since alkanes are almost non polar molecules because of the covalent in nature of carbon- carbon and carbon- hydrogen bond and very little difference of electronegativity between carbon and hydrogen atoms, therefore, these intermolecular force of attraction are of van der waals type which mainly depends upon the shape and hence the structure of the molecule. The magnitude of these forces of attraction depends upon the surface area of contact between adjacent molecules. Greater the surface area, stronger are the van der waals force of attraction. Let us now discuss the variation in physical properties of alkanes.

1. Nature: Due to the weak forces, C_1 to C_4 alkanes are gases that next 13 alkanes from C_5 to C_{17} are liquids and the higher members with more than 18 carbon atoms are solids at 298 K.

2. Boiling points: Alkanes have generally low boiling points because these are non- polar and the molecules are held together only by the weak van der waal's forces. With the increase in the number of carbon atoms, the molecular size increases and therefore, the magnitude of van der waals forces also increases. Consequently, the boiling point increases with increase in number of carbon atoms. it has been observed that each carbon atom added to the chain increases the boiling point by 20-30K . The below graph shows the variation of boiling points of n- alkanes with increase in number of carbon atoms per molecule of the homologous series.



Structure	Name	Boiling point (°C)
	pentane	36.0
	2-methylbutane	27.9
	2,2-dimethylpropane	9.5

The branched chain compounds have lower boiling point than the corresponding straight chain isomers as shown above. This is due to the fact that branching of the chain make the molecules more compact and thereby decrease the surface area. Therefore, the intermolecular attractive forces which depend upon the surface area also become small in magnitude on account of branching. Consequently, the boiling points of the branched chain alkanes are less than the straight chain isomers.

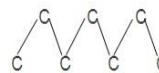
3. Melting points: The melting points of alkanes do not show regular variation with increase in molecular size. It has been observed that, in general, the alkanes with even number of carbon atoms have higher melting point than those with odd number of carbon atoms. This property is commonly known as alternation effect. The melting point of a substance depends not only upon the size and shape of the molecule but also upon the packing of its molecules in the crystal lattice. In n- alkane the carbon atoms are arranged in a zig zag chain. Therefore, in n- alkane containing an odd number of carbon atoms, the two terminal methyl group lie on the same side of zig zag

chain. On the other hand in case of n -alkane containing an even number of carbon atoms, the two terminal groups lie on the opposite side of the zig zag chain.

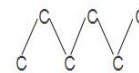
alkanes with odd number of carbons



alkanes with even number of carbons



odd number of carbon



even number of carbon

It is clear that alkanes with even number of carbon atoms have more symmetrical structures and result in closer packing in the crystal structure as compared to alkanes with odd number of carbon atoms. Therefore, the van der waals forces of attraction in the former are more and the melting points are higher as compared to the alkanes with odd number of carbon atoms.

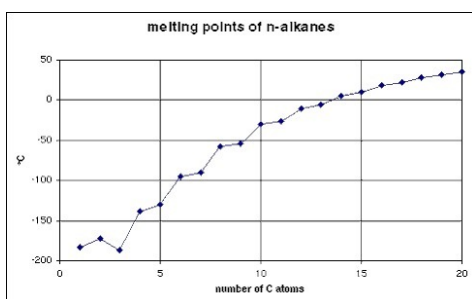


Table of Boiling Points of Linear Alkanes:

Name of Alkane	How many carbons ?	Chem Formula	Boiling Point in °C	State at (20°C)	Melting Point in °C
Methane	1	C ₁ H ₄	-162	gas	-183
Ethane	2	C ₂ H ₆	-89	gas	-172
Propane	3	C ₃ H ₈	-42	gas	-188
n-Butane	4	C ₄ H ₁₀	0	gas	-138
n-Pentane	5	C ₅ H ₁₂	36	liquid	-130
n-Hexane	6	C ₆ H ₁₄	69	liquid	-95
n-Heptane	7	C ₇ H ₁₆	98	liquid	-91
n-Octane	8	C ₈ H ₁₈	126	liquid	-57
n-Nonane	9	C ₉ H ₂₀	151	liquid	-54
n-Decane	10	C ₁₀ H ₂₂	174	liquid	-30

4. Solubility: 'like dissolves like' is the general rule of solubility. In the light of this rule, alkanes which are predominantly non-polar are insoluble in polar solvent such as water, alcohol etc. but are highly soluble in non-polar solvents such as petroleum ether, benzene, carbon tetrachloride etc. It may be noted here that greases are a mixture of higher alkanes and hence are non-polar and hydrophobic (water repelling) in nature. Similarly, petrol is a mixture of lower alkanes. Thus, both petrol and greases are non-polar. It is because of this reason that petrol is used for dry cleaning of clothes to remove grease stains.

5. Density: The density of alkane increase with increase in the molecular masses to the limiting value of about 0.8g cm⁻³ is reached. This means that all alkanes are lighter than water.

Assignment

- LPG mainly contains -----
 (A) methane (B) methane and ethane
 (C) hydrohen, methane and ethane (D) butane and isobutane
- Which of the following has the highest boiling point?
 (A) (CH₃)₄C (B) (CH₃)₂CHCH₃ (C) CH₃CH₂CH₂CH₂CH₃ (D) CH₃CH₂CH₂CH₃
- Isopropyl bromide on Wurtz reaction gives -----
 (A) hexane (B) propane (C) 2,3-dimethylbutane (D) neohexane
- Butene-1 may converted to butane by reaction with -----
 (A) Pd/H₂ (B) Zn-HCl (C) Sn-HCl (D) Zn-Hg

5. Pick out the alkane which differs from the other members of the group -----
 (A) 2,2-dimethylpropane (B) pentane (C) 3-methylbutane (D) 2,2-dimethylbutane
6. Alkyl halides react with dialkylcopper reagents to give -----
 (A) alkene (B) alkylcopper halide (C) alkane (D) alkenyl halides
7. An alkyl halide by formation of its Grignard reagent and heating with water gives propane. What is the original alkyl halide?
 (A) methyl iodide (B) ethyl iodide (C) ethyl bromide (D) propyl bromide
8. The number of structural isomers for C_6H_{14} is-----
 (A) 3 (B) 4 (C) 5 (D) 6
9. An alkane C_7H_{16} is produced by the reaction of lithium di(3-pentyl)cuprate with ethyl bromide. The structural formula of the product is -----
 (A) 3-ethylpentane (B) 2-methylpentane (C) 3-methylhexane (D) 2-methylhexane
10. Which of the following has the highest boiling point?
 (A) n-pentane (B) isopentane (C) neopentane (D) n-butane

1. (D) 2. (C) 3. (C) 4. (A) 5. (D) 6. (C) 7. (D) 8. (C) 9. (A) 10. (A)

ANSWERS