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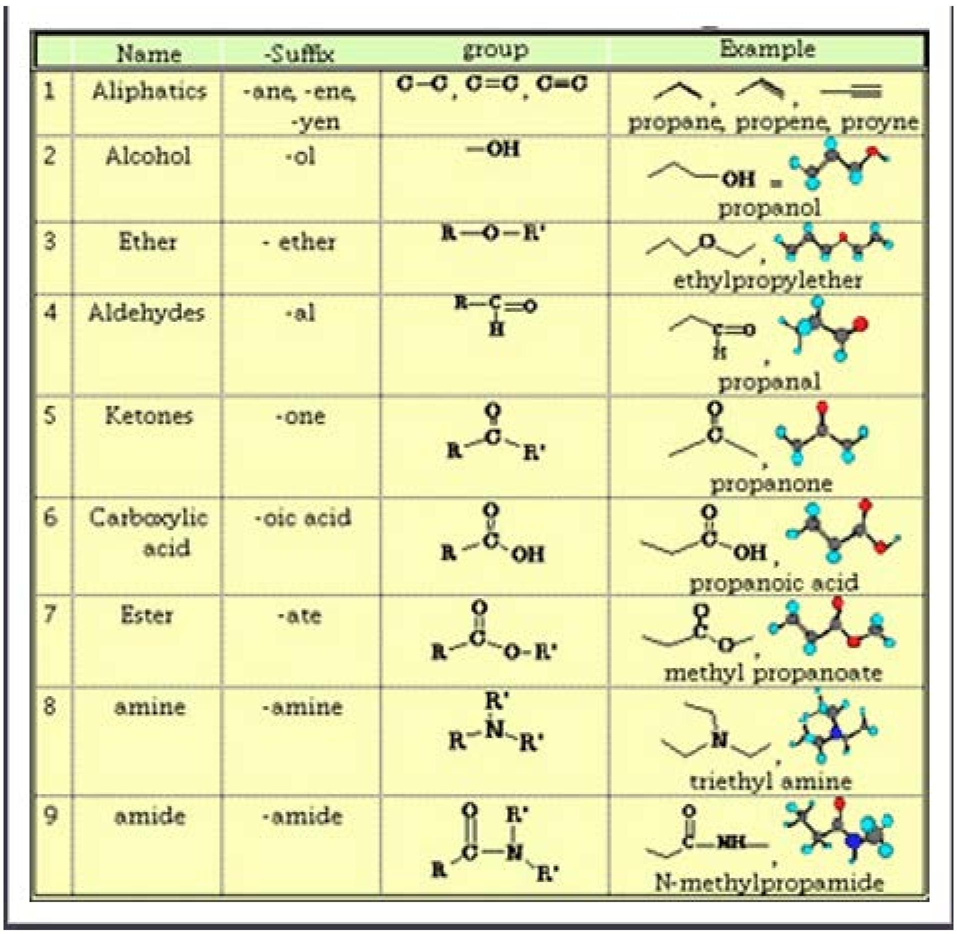
Hydrocarbon derivative

Hydrocarbon derivatives are compounds made up of carbon atoms and at least one other atom that is not hydrogen.

Table 1.11 Common Functional Groups



	Name	-Suffix	group	Example
1	Aliphatics	-ane, -ene, -yen	C–C, C=C, C≡C	propane, propene, proyne
2	Alcohol	-ol	–OH	propanol
3	Ether	- ether	R–O–R'	ethylpropylether
4	Aldehydes	-al	R–C(H)=O	propanal
5	Ketones	-one	R–C(=O)–R'	propanone
6	Carboxylic acid	-oic acid	R–C(=O)–OH	propanoic acid
7	Ester	-ate	R–C(=O)–O–R'	methyl propanoate
8	amine	-amine	R–N(R')–R'	triethyl amine
9	amide	-amide	R–C(=O)–N(R')–R'	N-methylpropamide

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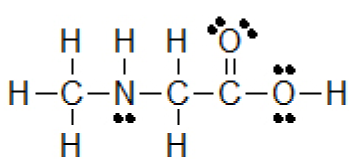
Drawing the Structure of Organic Molecules

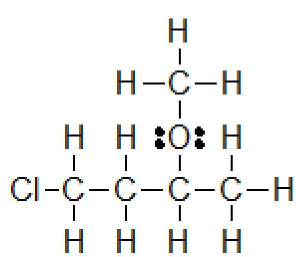
Structural Formulas - Lewis, Kekule, Bond-line, Condensed, & Perspective

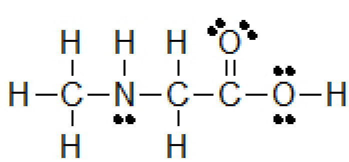
Shorthand notations to represent organic molecules rely on our knowledge of common neutral bonding patterns. Knowing these patterns, we can fill in the missing structural information. Some of these shorthand ways of drawing molecules give us insight into the bond angles and relative positions of atoms in the molecule, while some notations eliminate the carbon and hydrogen atoms and only indicate the heteroatoms (the atoms that are NOT carbon or hydrogen).

There are three primary methods to communicate chemical structure of organic molecules:

1-Kekule: Lewis structures using lines to represent covalent bonds and showing all atoms and lone pair electrons







Lone pairs remain as two electron dots, or are sometimes left out even though they are still there. Notice how the three lone pairs of electrons were not draw in around chlorine in example B.

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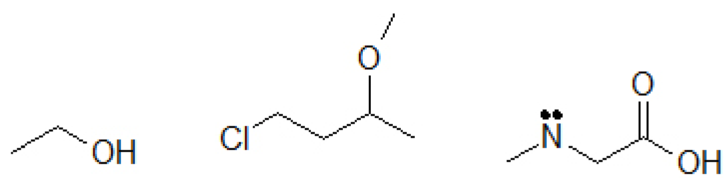
2-Bond-line (Skeletl-line): shows bonds between carbon atoms and heteroatoms) (with lone pair electrons when requested)

Bond-Line (a.k.a. zig-zag) Formulas

The name gives away how this formula works. This formula is full of bonds and lines, and because of the typical (more stable) bonds that atoms tend to make in molecules, they often end up looking like zig-zag lines. If you work with a molecular model kit you will find it difficult to make stick straight molecules (unless they contain sp triple bonds) whereas zig-zag molecules and bonds are much more feasible.



These molecules correspond to the exact same molecules depicted for Kekulé structures and condensed formulas. Notice how the carbons are no longer drawn in and are replaced by the ends and bends of a lines. In addition, the hydrogens have been omitted, but could be easily drawn in (see practice problems). Although we do not usually draw in the H's that are bonded to carbon, we do draw them in if they are connected to other atoms besides carbon (example is the OH group above in example A) . This is done because it is not always clear if the non-carbon atom is surrounded by lone pairs or hydrogens. Also in example A, notice how the OH is drawn with a bond to the second carbon, but it does not mean that there is a third carbon at the end of that bond/ line.

3-Condensed: all atoms are written to communicate structure without drawing any chemical bonds based on the carbon backbone

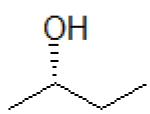
A condensed formula is made up of the elemental symbols. The order of the atoms suggests the connectivity. Condensed formulas can be read from either direction and H3C is the same as CH3, although the latter is more common because Look at the examples below and match them with their identical molecule under Kekulé structures and bond-line formulas.

(A) CH_3CH_2OH (B) $ClCH_2CH_2CH(OCH_3)CH_3$ (C) H_3CNHCH_2COOH

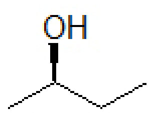
Let's look closely at example B. As you go through a condensed formula, you want to focus on the carbons and other elements that aren't hydrogen. The hydrogen's are important, but are usually there to complete octets. Also, notice the -OCH3 is in written in parentheses which tell you that it not part of the main chain of carbons. As you read through a a condensed formula, if you reach an atom that doesn't have a complete octet by the time you reach the next hydrogen, then it's possible that there are double or triple bonds. In example C, the carbon is double bonded to oxygen and single bonded to another oxygen. Notice how COOH means C(=O)-O-H instead of CH3-C-O-O-H because carbon does not have a complete octet and oxygens.

Dashed-Wedged Line Structure

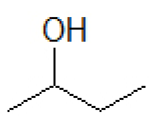
As you may have guessed, the Dashed-Wedged Line structure is all about lines, dashes, and wedges. At first it may seem confusing, but with practice, understanding dash-wedged line structures will become like second nature. The following are examples of each, and how they can be used together.



Dashed



Wedged



Line

Dashed-Wedged Line

==

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ALKANES

IUPAC naming system:

Molecular formula	Condensed Structural Formula	Name
CH_4	CH_4	**methane**
C_2H_6	CH_3CH_3	**ethane**
C_3H_8	$CH_3CH_2CH_3$	**propane**
C_4H_{10}	$CH_3CH_2CH_2CH_3$	**butane**
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	**pentane**
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	**hexane**
C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	**heptane**
C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	**octane**
C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	**nonane**
$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	**decane**

Physical Properties of Alkanes

- Solubility: Alkanes are hydrophobic and dissolve in nonpolar or weakly polar solvents.
- Density: Alkanes are less dense than water. Mixtures of alkanes and water separate into two phases with the alkane on top.
- Boiling Points: Alkane bp increase by 20-30 ^{0} with each additional CH_2 (methylene group). For a group of isomeric alkanes, the bp decreases with branching due to an overall decrease in surface area.

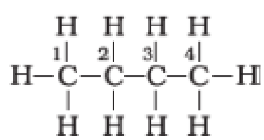
Nomenclature and Isomerism

Nomenclature and Isomerism

Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes

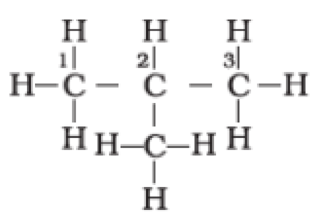
– methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C4H10. Four carbon atoms of C4H10 can be joined either in a continuous chain or with a branched chain in the following two ways :

I



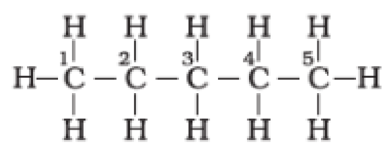
Butane (*n*- butane).

II



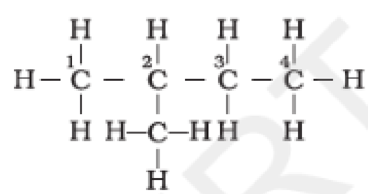
2-Methylpropane (isobutane)

III



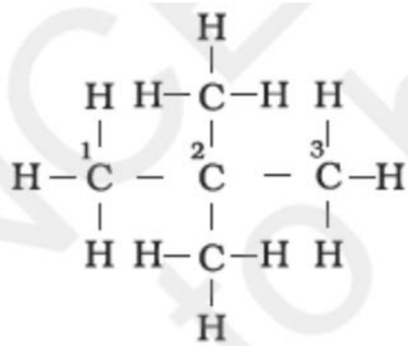
Pentane (*n*-pentane)

IV



2-Methylbutane (isopentane)

V

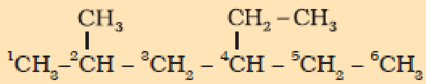
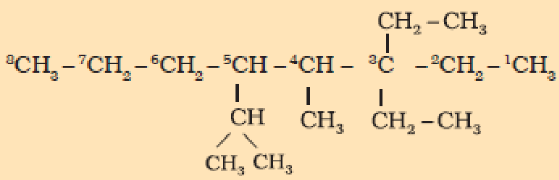
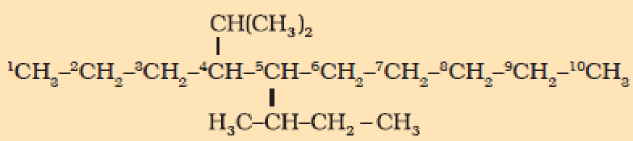
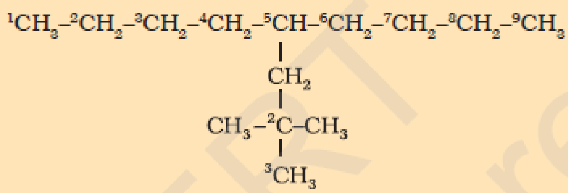
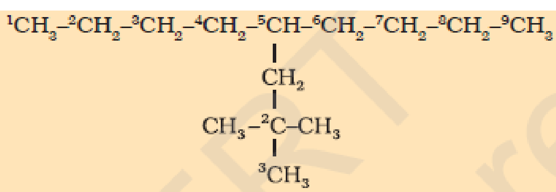
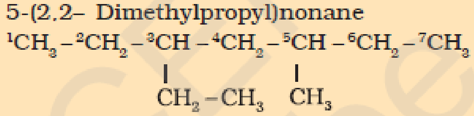


2.2-Dimethylpropane (neopentane)

structures, they are known as **structural isomers**. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as **chain isomers**. Thus, you have seen that C_4H_{10} and C_5H_{12} have two and three chain isomers respectively.

Problem 13.1

Write structures of different chain isomers of alkanes corresponding to the molecular formula C_6H_{14}. Also write their IUPAC names.

Structure and IUPAC Name	Remarks
(a)  (4 – Ethyl – 2 – methylhexane)	Lowest sum and alphabetical arrangement
(b)  (3,3-Diethyl-5-isopropyl-4-methyloctane)	Lowest sum and alphabetical arrangement
(c)  5-*sec*– Butyl-4-isopropyldecane	*sec* is not considered while arranging alphabetically; isopropyl is taken as one word
(d) 	Further numbering to the substituents of the side chain
(d)  5-(2,2– Dimethylpropyl)nonane	Further numbering to the substituents of the side chain
(e)  3–Ethyl–5–methylheptane	Alphabetical priority order

Problem 13.3

Write IUPAC names of the following compounds :

(i) $(CH_3)_3\,C\,CH_2C(CH_3)_3$

(ii) $(CH_3)_2\,C(C_2H_5)_2$

(iii) tetra – *tert*-butylmethane

Solution

(i) 2, 2, 4, 4-Tetramethylpentane

(ii) 3, 3-Dimethylpentane

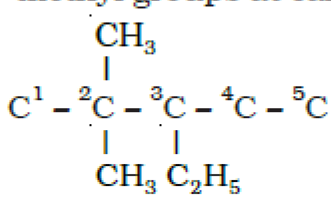
(iii) 3,3-Di-*tert*-butyl -2, 2, 4, 4 - tetramethylpentane

If it is important to write the correct IUPAC name for a given structure, it is equally important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2, 2–dimethylpentane in the following steps :

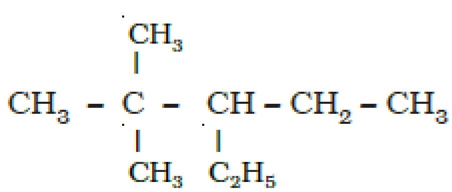
i) Draw the chain of five carbon atoms: C – C – C – C – C

ii) Give number to carbon atoms: $C^1 – C^2 – C^3 – C^4 – C^5$

iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2



iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms :



Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems.

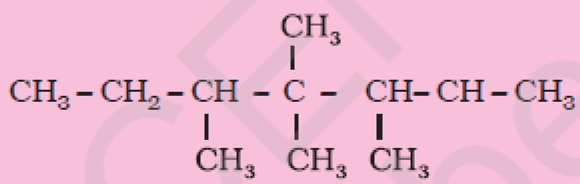
Problem 13.4

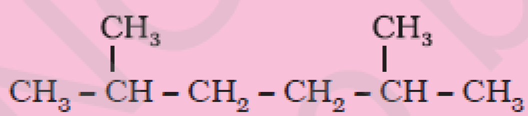
Write structural formulas of the following compounds :

(i) 3. 4. 4. 5–Tetramethylheptane

(ii) 2.5-Dimethyhexane

Solution

(i) 

(ii) 

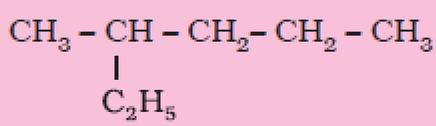
Problem 13.5

Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names.

(i) 2-Ethylpentane

(ii) 5-Ethyl – 3-methylheptane

Solution

(i) 

Longest chain is of six carbon atoms and not that of five. Hence, correct name is 3-Methylhexane.

$$\text{(ii)}\quad \overset{7}{CH_3}-\overset{6}{CH_2}-\underset{\displaystyle CH_3}{\overset{5}{CH}}-\overset{4}{CH_2}-\underset{\displaystyle C_2H_5}{\overset{3}{CH}}-\overset{2}{CH_2}-\overset{1}{CH_3}$$

Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane.

Preparation of alkanes

1- Hydrogenation of unsaturated hydrocarbon:

$$H_2C{=}CH_2 \xrightarrow[200,\ 300]{\text{Ni or Pd or Pt / } H_2} H_3C{-}CH_3$$

2- Hydrolysis of Grignard reagent

- i) R—X + Mg → RMgX (Grignard reagent)
- ii) RMgX + H_2O → RH + Mg(OH)X

$$CH_3CH_2Br + Mg^{2+} \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

$$CH_3CH_2MgBr \xrightarrow{H_3O^+} CH_3CH_3 + Mg(OH)Br$$

3- Reduction of alkyl halide

A-

i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

For eg:

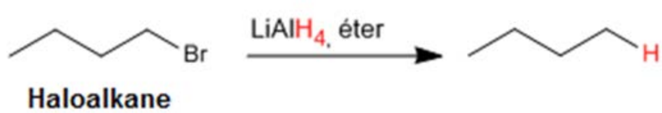
$$CH_3-Cl + H_2 \xrightarrow{Zn,\ H^+} CH_4 + HCl$$

Chloromethane — Methane

$$C_2H_5-Cl + H_2 \xrightarrow{Zn,\ H^+} C_2H_6 + HCl$$

Chloroethane — Ethane

B- Reduction by using LiAlH4, ether



4-Wurtz reaction

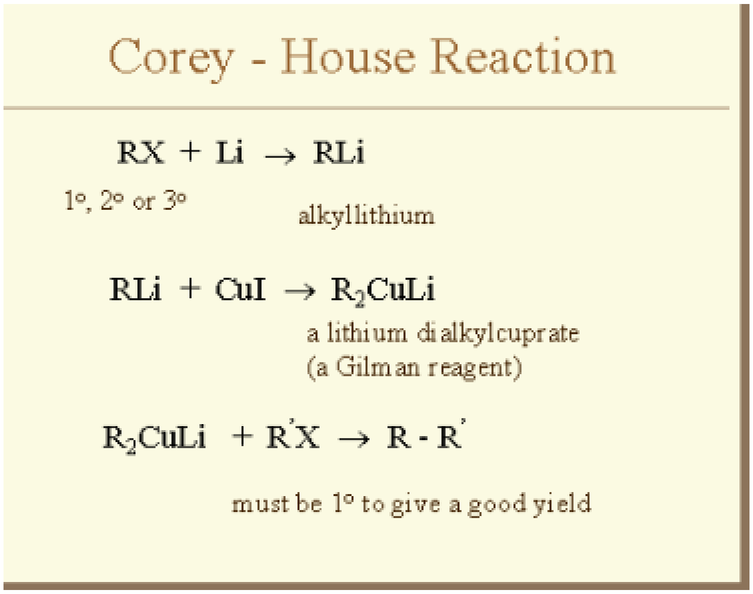
Wurtz reaction

$$C_2H_5I + 2Na + CH_3I \xrightarrow{\text{Dry ether}} C_2H_5 - CH_3 + 2NaI$$

$$2\ C_2H_5I + 2Na \xrightarrow{\text{Dry ether}} C_2H_5I - C_2H_5 + 2NaI$$

$$2\ CH_3I + 2Na \xrightarrow{\text{Dry ether}} CH_3 - C_2H_5 + 2NaI$$

5- Corey-House Reaction



<u>Reaction of Alkanes</u>

1- <u>Hlogenation of Alkanes</u>

a Halogenation of Alkanes:

Substitution reaction (radical halogenations): Alkanes react with halogens to produce alkyl halides. The reaction is catalyzed by light or heat.

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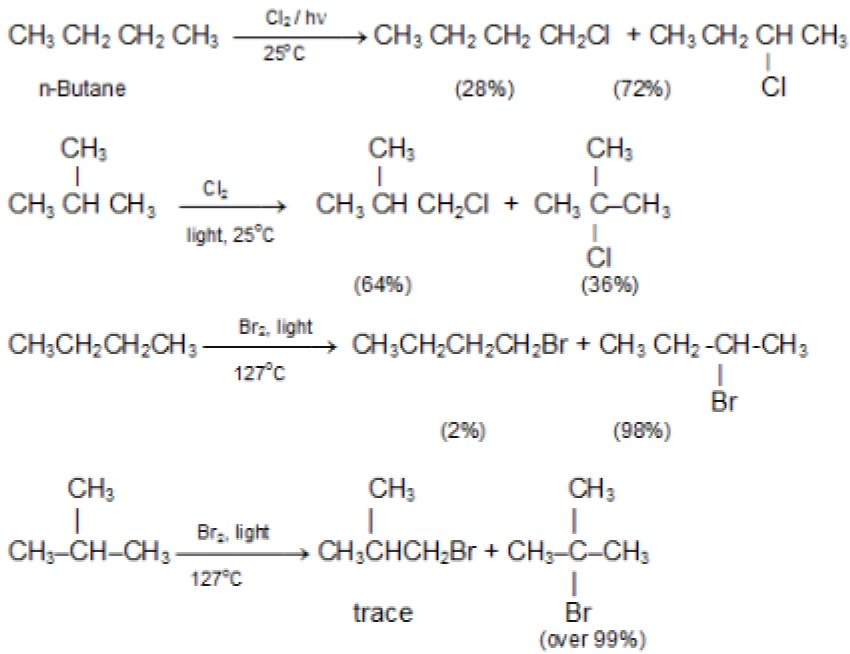
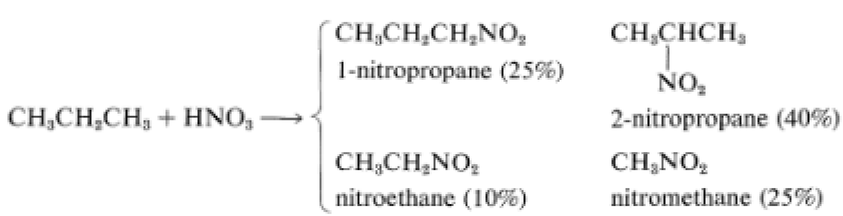


2-Nitration of alkanes



3-Combustion

Complete Combustion

In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO_2 and H_2O.

$C_8H_{18}(g) + 12.5\ O_2(g) \rightarrow 8CO_2(g) + 9\ H_2O(l)$

4- Reaction with CH_2CO