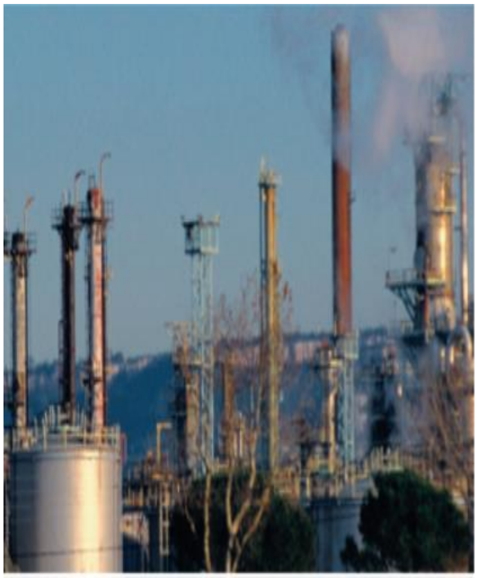


Chapter 2

Alkanes and Cycloalkanes; Conformational and Geometrical Isomerism

- **Hydrocarbons** are compounds that contain only carbon and hydrogen.

There are three main classes of hydrocarbons, based on the types of carbon–carbon bonds present.

1-**Saturated hydrocarbons** contain only carbon–carbon *single* bonds.

2-**Unsaturated hydrocarbons** contain carbon–carbon *multiple* bonds, double bonds, triple bonds, or both.

3-**Aromatic hydrocarbons** are a special class of cyclic compounds related in structure to benzene.

- Saturated hydrocarbons are known as **alkanes** if they are acyclic, or as
- **cycloalkanes** if they are cyclic.

2.1 The Structure of Alkanes

- Alkanes are hydrocarbons containing only single saturated bonds. General formula: C_nH_{2n+2}.

- The simplest alkane is methane.
- Its tetrahedral three-dimensional structure .

- Alkanes with carbon chains that are unbranched are called **normal alkanes** or *n*-alkanes.
- Each member of this series differs from the next higher and the next lower member by a -CH_2-group (called a **methylene group**).
- A series of compounds in which the members are built up in a regular, repetitive way like this is called a **homologous series**.

Table 2.1 Names and Formulas of the First Ten Unbranched Alkanes

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

- Compounds of a **homologous series** differ by *a regular unit* of structure and share *similar properties*.

- **PROBLEM 2.2** Which of the following are alkanes?

a. C_7H_{16}

b. C_7H_{12}

c. C_8H_{16}

d. $C_{29}H_{60}$

2.2 Nomenclature of organic compounds

- In the early days of organic chemistry, each new compound was given a name that was usually based on its source or use.

 Examples include
 limonene (from lemons), α-pinene (from pine trees), coumarin (from the tonka bean, known to South American natives as *cumaru*)

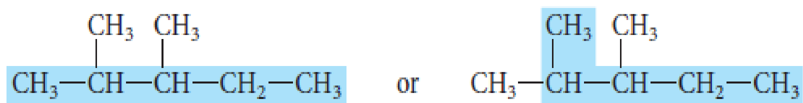
- Internationally recognized systems of nomenclature were devised by a commission of the International Union of Pure and Applied Chemistry; they are known as the IUPAC

2.3 IUPAC rules for naming alkanes

1. The general name for acyclic saturated hydrocarbons is *alkanes*. The -***ane*** ending is used for all saturated hydrocarbons. This is important to remember because later other endings will be used for other functional groups.

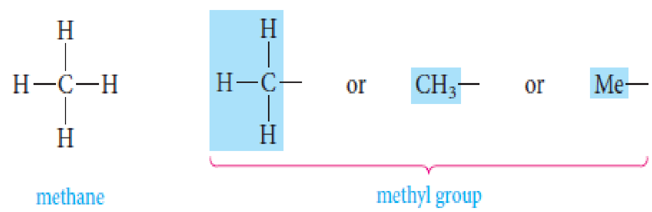
2. Alkanes without branches are named according to the *number of carbon atoms*. These names, up to ten carbons, are given in the first column of Table 2.1.

3. For alkanes with branches, the **root name** is that of the longest continuous chain of carbon atoms. For example, in the structure



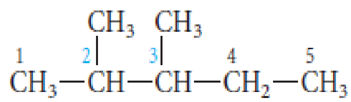
the longest continuous chain (in color) has five carbon atoms. The compound is therefore named as a substituted *pent*ane, even though there are seven carbon atoms altogether.

4. Groups attached to the main chain are called **substituents**. Saturated substituents that contain only carbon and hydrogen are called **alkyl groups**. An alkyl group is named by taking the name of the alkane with the same number of carbon atoms and changing the *-ane* ending to *-yl*.



5. The main chain is numbered in such a way that the first substituent encountered along the chain receives the lowest possible number. Each substituent is then located by its name and by the number of the carbon atom to which it is attached.

- When two or more identical groups are attached to the main chain, prefixes such as *di-, tri-*, and *tetra-* are used. *Every substituent must be named and numbered,* even if two identical substituents are attached to the same carbon of the main chain.



2,3-dimethylpentane

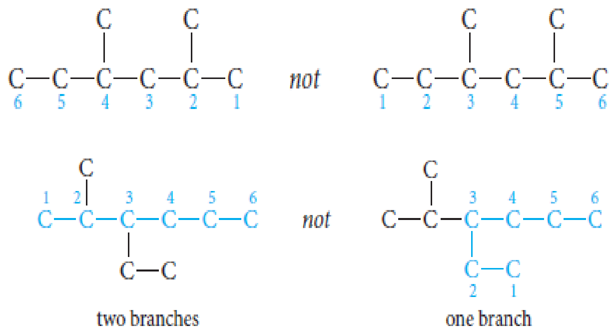
6. If two or more different types of substituents are present, they are listed alphabetically, except that prefixes such as *di*- and *tri*- are not considered when alphabetizing.

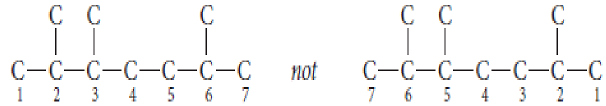
7. Punctuation is important when writing IUPAC names. IUPAC names for hydrocarbons are written as one word. Numbers are separated from each other by commas and are separated from letters by hyphens. There is no space between the last named substituent and the name of the parent alkane that follows it.

notes

1. Locate the longest continuous carbon chain. This gives the name of the parent hydrocarbon. For example,

2. Number the longest chain beginning at the end nearest the first branch point. For example,





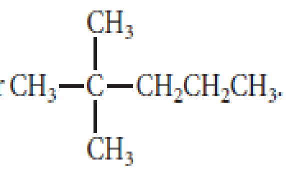
2,3,6-trimethylheptane *not* 2,5,6-trimethylheptane

3-ethyl-5-methylheptane *not* 5-ethyl-3-methylheptane

3. Write the name as one word, placing substituents in alphabetic order and using proper punctuation.

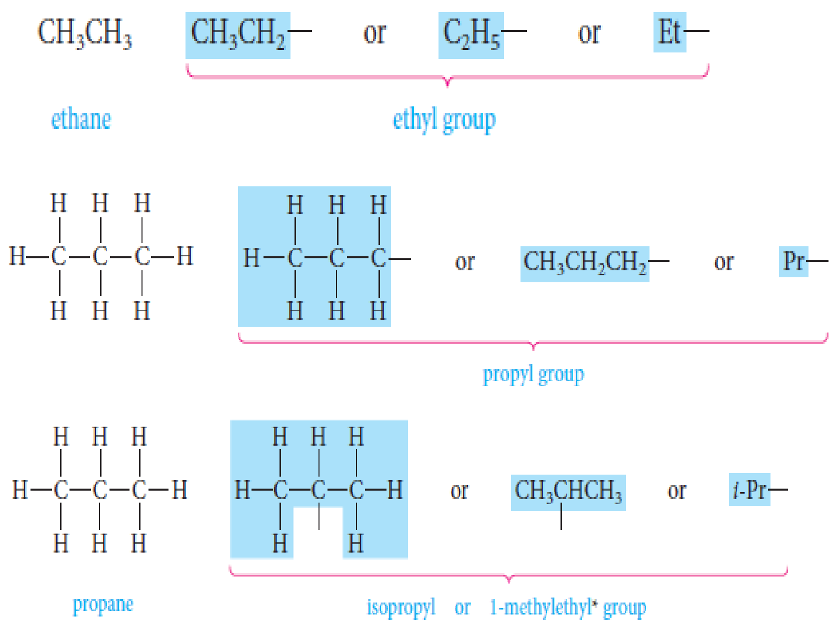
Example 2.2

Give an IUPAC name for



2,2-dimethylpentane

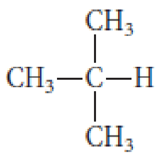
2.4 Alkyl and Halogen Substituents



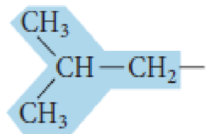
and

butyl

sec-butyl
(or 1-methylpropyl)

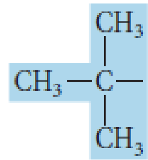


isobutane



isobutyl
(or 2-methylpropyl)

and



tert-butyl
(or 1,1-dimethylethyl)

R is the general symbol for an alkyl group.

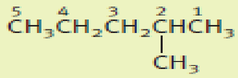
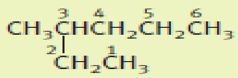
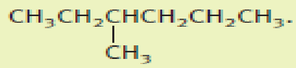
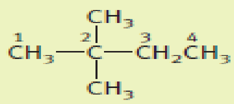
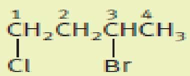
Halogen substituents are named by changing the *-ine* ending of the element to *-o*.

F-	Cl-	Br-	I-
fluoro-	chloro-	bromo-	iodo-

Give the common and IUPAC names for $CH_3CH_2CH_2Br$.

2.5 Use of the IUPAC Rules

Table 2.2 — Examples of Use of the IUPAC Rules

 2-methylpentane (*not* 4-methylpentane)	The ending *-ane* tells us that all the carbon–carbon bonds are single; *pent-* indicates five carbons in the longest chain. We number them from right to left, starting closest to the branch point.
 3-methylhexane (*not* 2-ethylpentane or 4-methylhexane)	This is a six-carbon saturated chain with a methyl group on the third carbon. We would usually write the structure as .
 2,2-dimethylbutane (*not* 2,2-methylbutane or 2-dimethylbutane)	There must be a number for each substituent, and the prefix *di-* says that there are two methyl substituents.
 3-bromo-1-chlorobutane (*not* 1-chloro-3-bromobutane or 2-bromo-4-chlorobutane)	First, we number the butane chain from the end closest to the first substituent. Then we name the substituents in alphabetical order, regardless of position number.

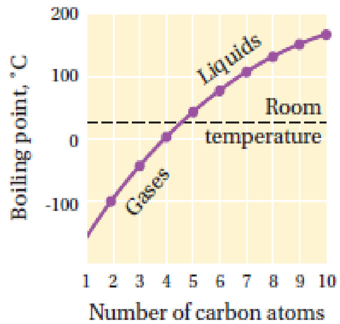
- **PROBLEM 2.8**

Explain why 1,3-difluorobutane is a correct IUPAC name, but 1,3-dimethylpentane is *not* a correct IUPAC name.

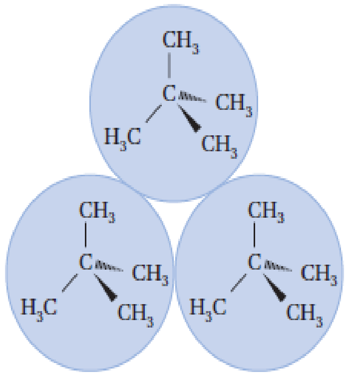
2.7 Physical properties and Intermolecular Interactions

- Alkanes are insoluble in water. That is because water molecules are polar, whereas alkanes are nopolar. (all C-C and C-H bonds are nearly purely covalent.)
- Alkanes have lower boiling points for a given molecular weight than most other organic compounds. The electrons in a nonpolar molecule can become unevenly distributed within the molecule, causing the molecule to have partially positive and partially negative end. The temporarily polarized molecules causes its neighbor molecules polarized as well. Such interaction are called **Van der Waals attraction.**

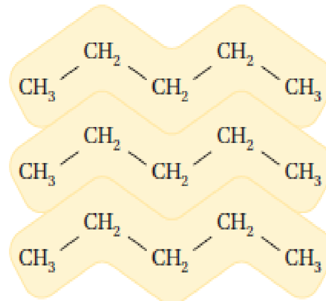
- The boiling points for alkanes rise as the chain length increases and fall as the chains become branched and more nearly spherical in shape.



Name	Formula	Boiling point, °C
pentane	$CH_3CH_2CH_2CH_2CH_3$	36
2-methylbutane (isopentane)	$CH_3CH(CH_3)CH_2CH_3$	28
2,2-dimethyl-propane (neopentane)	$C(CH_3)_4$	10



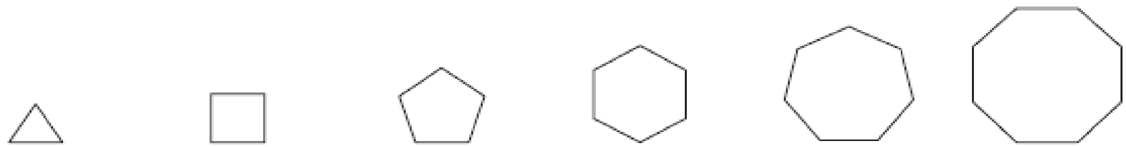
2,2-dimethylpropane
bp 10˚C



pentane
bp 36˚C

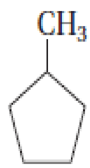
2.9 Cycloalkanes Nomenclature and Conformation

- Cycloalkanes are saturated hydrocarbons that have at least one ring of carbon atoms.
- Cycloalkanes are named by placing the prefix *cyclo*- before the alkane name that corresponds to the number of carbon atoms in the ring.

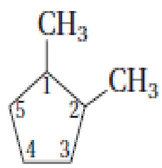


cyclopropane	cyclobutane	cyclopentane	cyclohexane	cycloheptane	cyclooctane
bp −32.7°C	bp 12°C	bp 49.3°C	bp 80.7°C	bp 118.5°C	bp 149°C

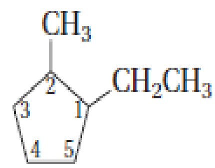
- Nomenclature
- Alkyl or halogen substituents attached to the rings are named in the usual way.
- If only one substituent is present, no number is needed to locate it.
- If there are several substituents , numbers are required. One substituent is always located at ring carbon number 1, and the remaining ring carbons are then numbered consecutively in a way that gives the other substituents the lowest possible numbers



methylcyclopentane
(*not* 1-methylcyclopentane)

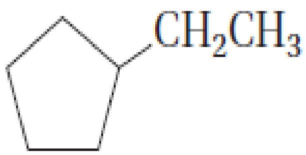


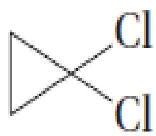
1,2-dimethylcyclopentane
(*not* 1,5-dimethylcyclopentane)

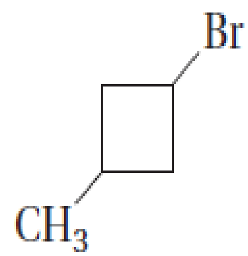


1-ethyl-2-methylcyclopentane
(*not* 2-ethyl-1-methylcyclopentane)

PROBLEM 2.12 Give IUPAC names for

a. 

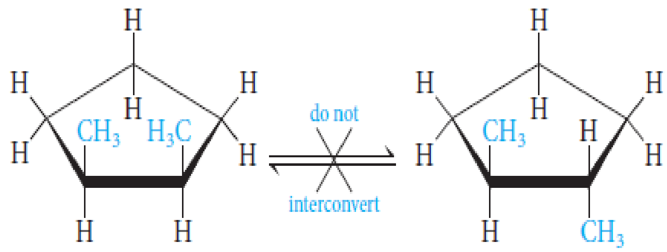
b. 

c. 

a. ethylcyclopentane
b. 1,1-dichlorocyclopropane
c. 1-bromo-3-methylcyclobutane

2.10 *Cis-Trans* Isomerism in Cycloalkanes

- **Stereoisomerism** deals with molecules that have the same order of attachment of the atoms, but different arrangements of the atoms in space. ***Cis–trans* isomerism** (sometimes called **geometrical isomerism**) is one kind of stereoisomerism, and it is most easily understood with a specific case.



cis-1,2-dimethylcyclopentane
bp 99°C

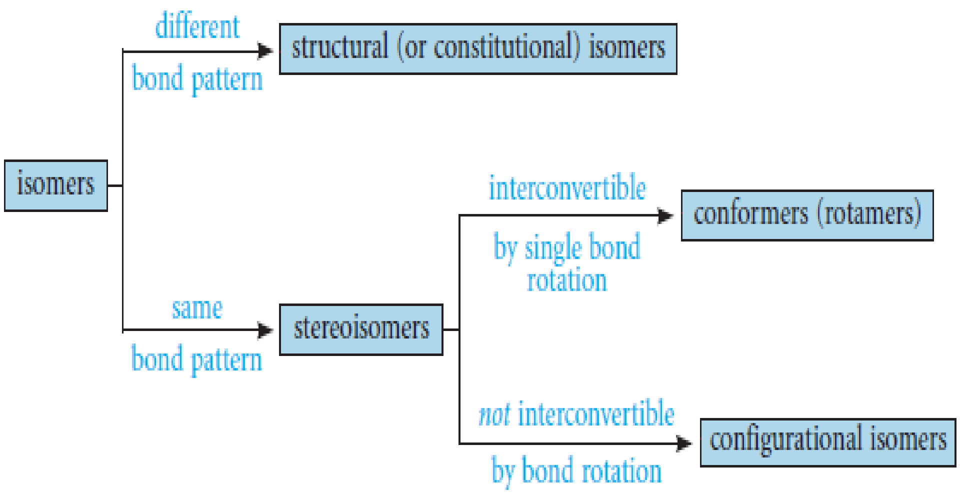
trans-1,2-dimethylcyclopentane
bp 92°C

- *Cis*: like groups on same side of ring
- *Trans*: like groups on opposite sides of ring

PROBLEM 2.16 Draw the structure for the *cis* and *trans* isomers of

a. 1,3-dibromocyclopentane
b. 1-chloro-2-methylcyclopropane

2.11 Summery of Isomerism



PROBLEM 2.17 Classify each of the following isomer pairs according to the scheme

- a. *cis*- and *trans*-1,2-dimethylcyclohexane
- b. chair and boat forms of cyclohexane
- c. 1-fluoropropane and 2-fluoropropane

2.12 Reactions of Alkanes

- All of the bonds in alkanes are single, covalent, and nonpolar. Hence alkanes are relatively inert.
- Because of this inertness, alkanes can be used as solventsfor extraction or crystallization as well as for carrying out chemical reactions of other substances.

1) Oxidation and Combustion: alkanes as fuels

$$\underset{\text{methane}}{CH_4} + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O + \text{heat}\ (212.8\ \text{kcal/mol})$$

$$\underset{\text{butane}}{C_4H_{10}} + \tfrac{13}{2}\,O_2 \longrightarrow 4\,CO_2 + 5\,H_2O + \text{heat}\ (688.0\ \text{kcal/mol})$$

Partial oxidation of hydrocarbon

$$2\,CH_4 + 3\,O_2 \longrightarrow \underset{\text{carbon monoxide}}{2\,CO} + 4\,H_2O$$

$$CH_4 + O_2 \longrightarrow \underset{\text{carbon}}{C} + 2\,H_2O$$

$$CH_4 + O_2 \longrightarrow \underset{\text{formaldehyde}}{CH_2O} + H_2O$$

$$2\,C_2H_6 + 3\,O_2 \longrightarrow \underset{\text{acetic acid}}{2\,CH_3CO_2H} + 2\,H_2O$$

2.12 b Halogenation of alkanes.

- General formula $$\mathrm{R{-}H + Cl{-}Cl \xrightarrow[\text{heat}]{\text{light or}} R{-}Cl + H{-}Cl}$$

For methane

$$\underset{\text{methane}}{\mathrm{CH_4}} + \mathrm{Cl{-}Cl} \xrightarrow[\text{or heat}]{\text{sunlight}} \underset{\substack{\text{chloromethane} \\ \text{(methyl chloride)} \\ \text{bp } -24.2^\circ\text{C}}}{\mathrm{CH_3Cl}} + \mathrm{HCl}$$

- The reaction is called **chlorination**. This process is a **substitution reaction**, as a chlorine is substituted for a hydrogen . An analogous reaction, called **bromination**, occurs when the halogen source is bromine.

$$\mathrm{R{-}H + Br{-}Br \xrightarrow[\text{heat}]{\text{light or}} R{-}Br + HBr}$$

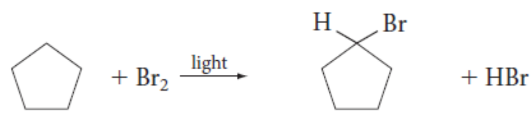
- If excess halogen is present, the reaction can continue further to give polyhalogenated products. Thus, methane and excess chlorine can give products with two, three, or four chlorines

$$CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

CH_2Cl_2	$CHCl_3$	CCl_4
dichloromethane	trichloromethane	tetrachloromethane
(methylene chloride)	(chloroform)	(carbon tetrachloride)
bp 40°C	bp 61.7°C	bp 76.5°C

$$CH_3CH_2CH_3 + Cl_2 \xrightarrow[\text{or heat}]{\text{light}} CH_3CH_2CH_2Cl + CH_3\underset{\underset{Cl}{|}}{C}HCH_3 + HCl$$

propane → 1-chloropropane (*n*-propyl chloride) + 2-chloropropane (isopropyl chloride)

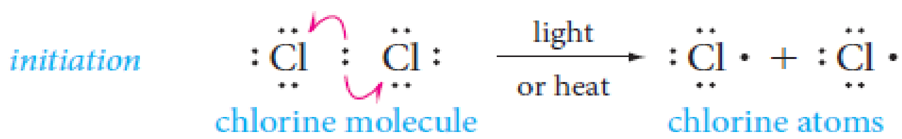


cyclopentane

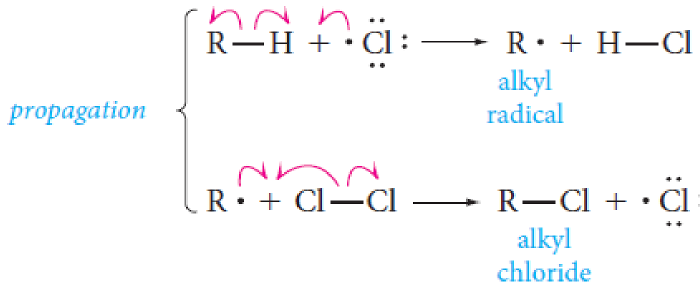
bromocyclopentane (cyclopentyl bromide)

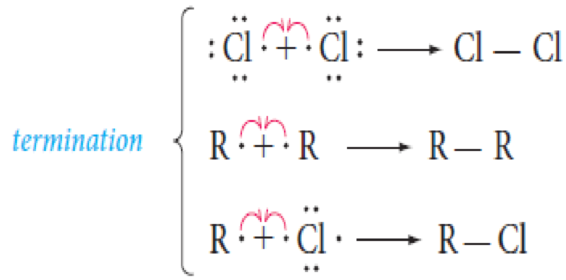
2.13 Free Radical Chain Mechanism of Halogenation

- A **reaction mechanism** is a step-by-step description of the bond-breaking and bond-making processes that occur when reagents react to form products. In the case of halogenation, various experiments show that this reaction occurs in several steps , and not in one magical step. Indeed, halogenation occurs via a **free-radical chain** of reactions.
- The **chain-initiating step** is the breaking of the halogen molecule into two halogen atoms.



The **chain-propagating steps** are





mechanism for the monochlorination of methane