ORGANIC CHEMISTRY

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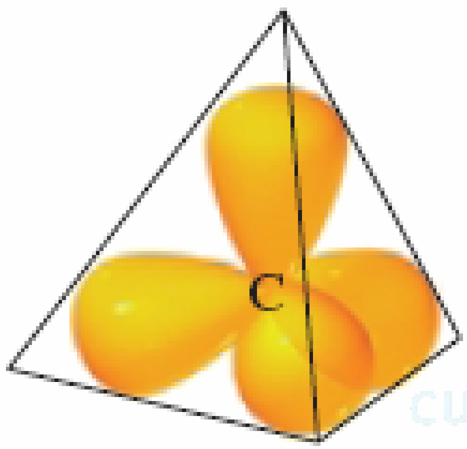
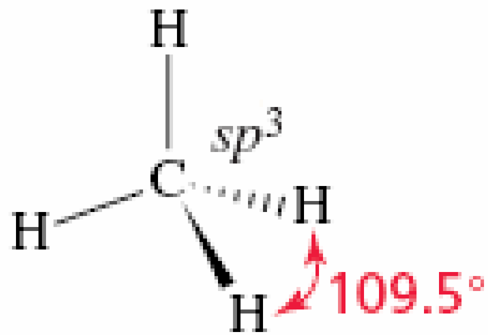
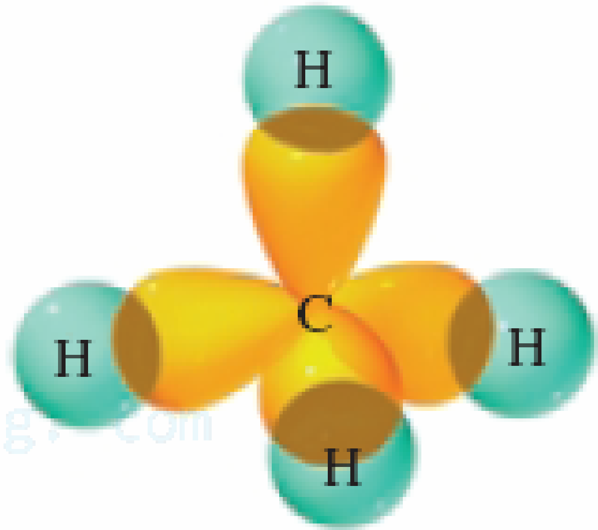
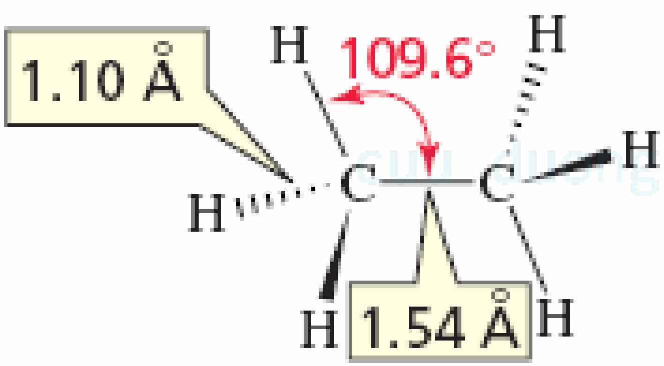
Chapter 4: ALKANES



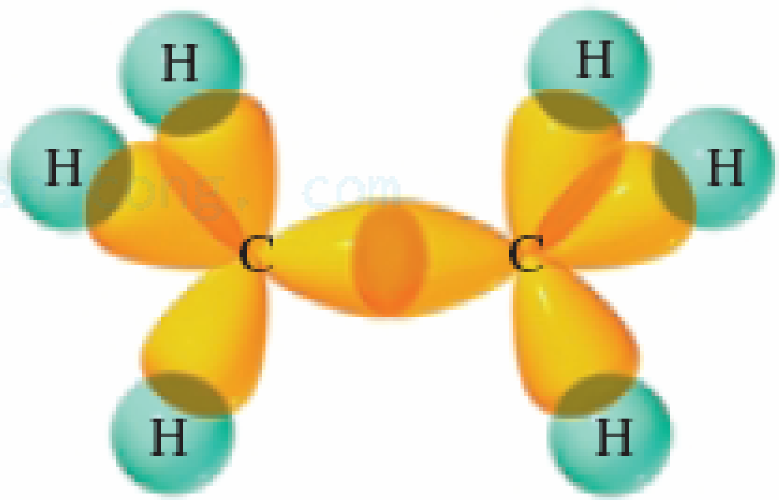


perspective formula of methane





perspective formula of ethane



NOMENCLATURE OF ALKANES

IUPAC Names of Unbranched Alkanes

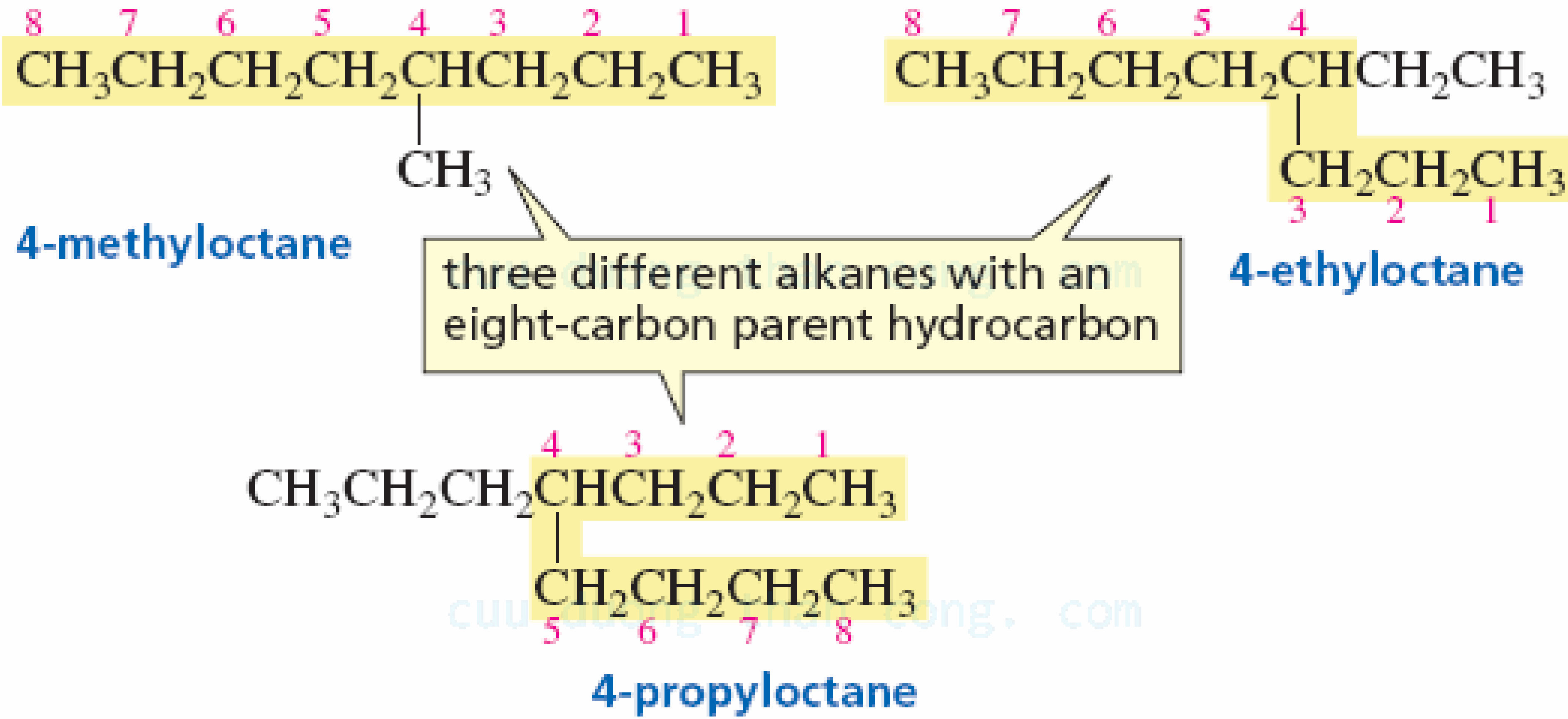
Number of carbon atoms	Name	Number of carbon atoms	Name	Number of carbon atoms	Name
1	Methane	11	Undecane	21	Henicosane
2	Ethane	12	Dodecane	22	Docosane
3	Propane	13	Tridecane	23	Tricosane
4	Butane	14	Tetradecane	24	Tetracosane
5	Pentane	15	Pentadecane	30	Triacontane
6	Hexane	16	Hexadecane	31	Hentriacontane
7	Heptane	17	Heptadecane	32	Dotriacontane
8	Octane	18	Octadecane	40	Tetracontane
9	Nonane	19	Nonadecane	50	Pentacontane
10	Decane	20	Icosane*	100	Hectane

ALKYL SUBSTITUENTS

Names of Some Alkyl Groups

methyl	$CH_3—$	*sec*-butyl	$CH_3CH_2\underset{\substack{\mid\\ CH_3}}{CH}—$
ethyl	$CH_3CH_2—$		
propyl	$CH_3CH_2CH_2—$		
isopropyl	$CH_3\underset{\substack{\mid\\ CH_3}}{CH}—$	*tert*-butyl	$CH_3\overset{\substack{CH_3\\ \mid}}{\underset{\substack{\mid\\ CH_3}}{C}}—$
butyl	$CH_3CH_2CH_2CH_2—$	pentyl	$CH_3CH_2CH_2CH_2CH_2—$
isobutyl	$CH_3\underset{\substack{\mid\\ CH_3}}{CH}CH_2—$	isopentyl	$CH_3\underset{\substack{\mid\\ CH_3}}{CH}CH_2CH_2—$

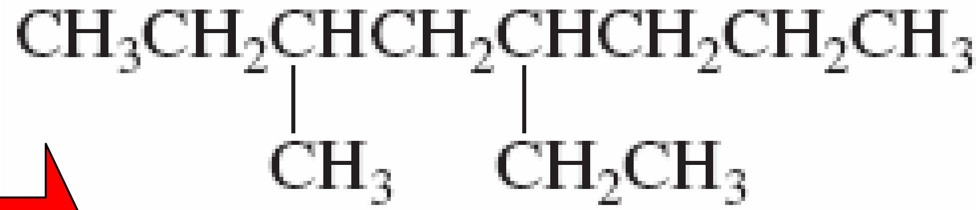
IUPAC NAMES OF BRANCHED ALKANES



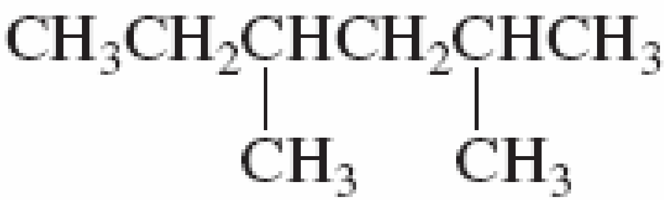
Determine the parent hydrocarbon – the longest continuous carbon chain

- **Substituents are listed in alphabetical order**

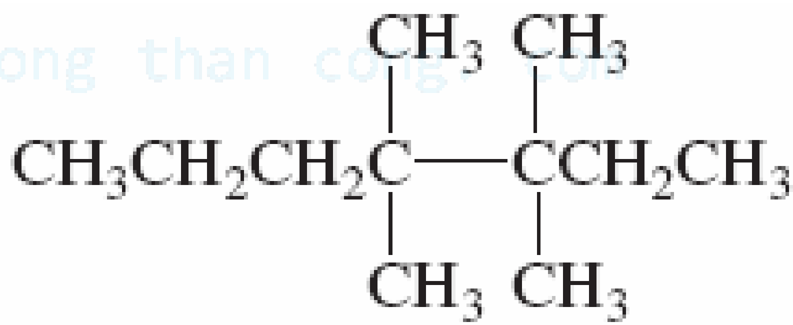
- **Carbon chain is numbered with the lowest possible number in the compound**



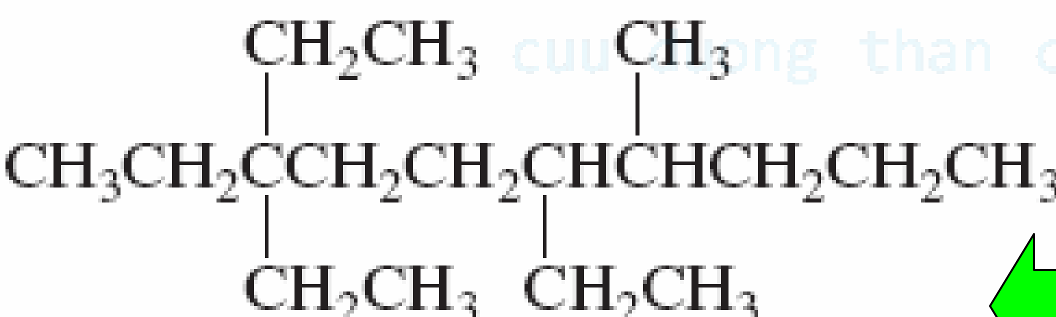
5-ethyl-3-methyloctane
not
4-ethyl-6-methyloctane
because 3 < 4



2,4-dimethylhexane

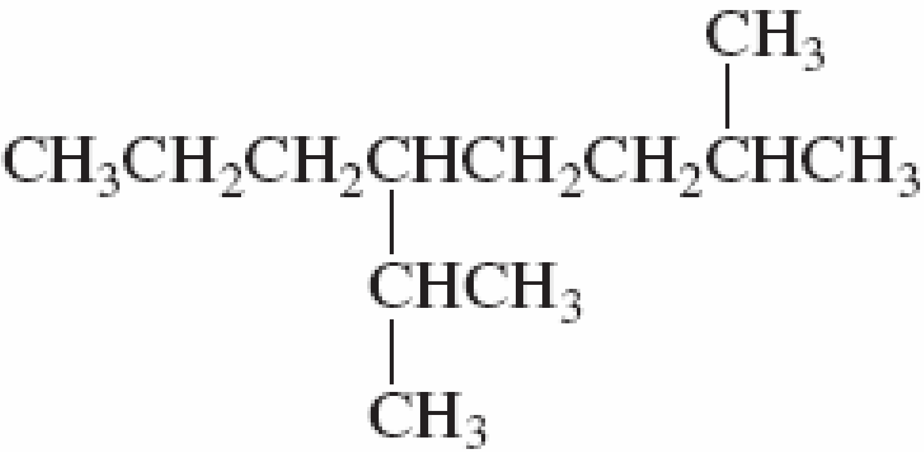


3,3,4,4-tetramethylheptane

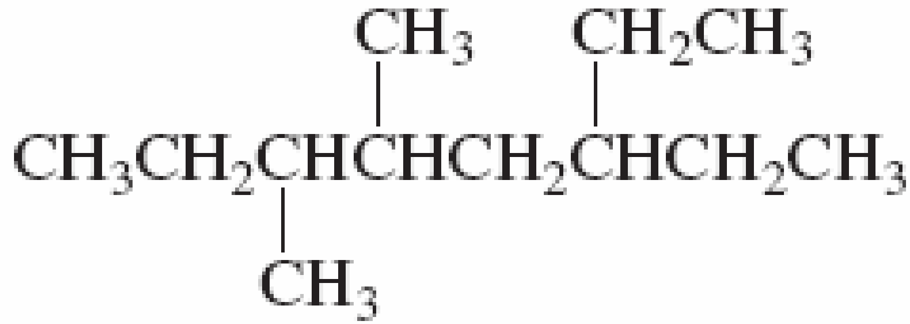


3,3,6-triethyl-7-methyldecane

Substituents are the same

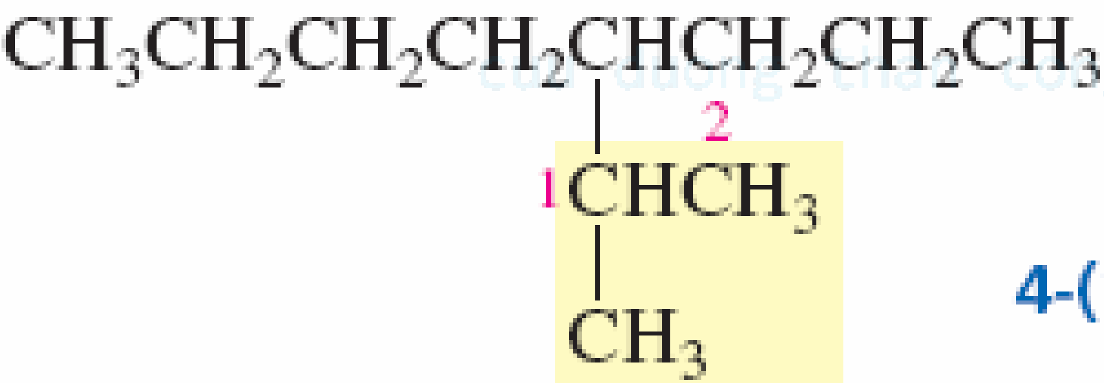


5-isopropyl-2-methyloctane

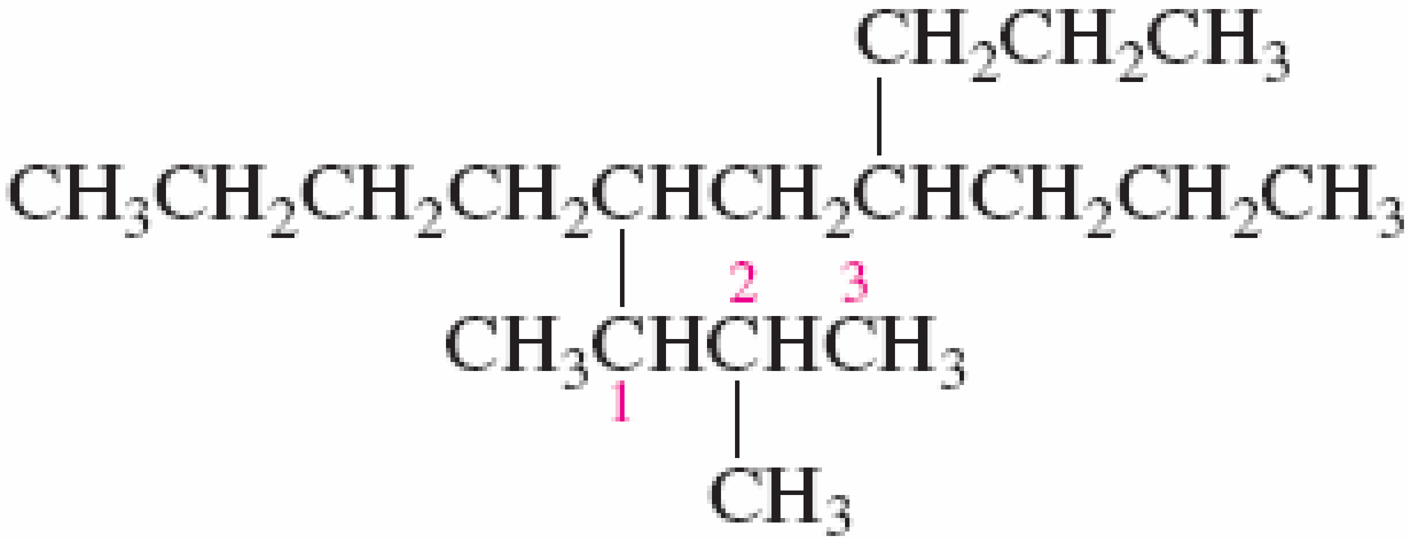


6-ethyl-3,4-dimethyloctane

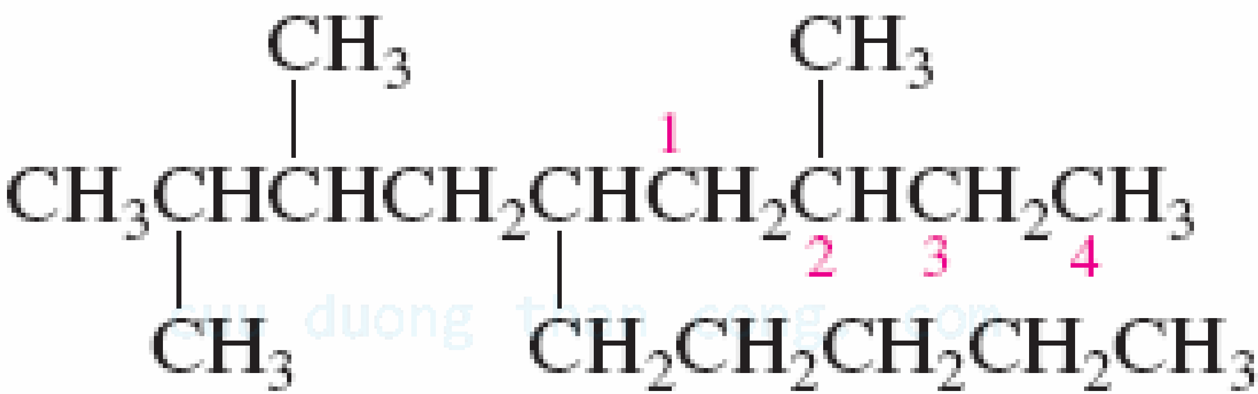
- ***Di, tri, tetra, n, sec*, and *tert* are ignored in alphabetizing substituents**
- ***Iso, neo,* and *cyclo* are not ignored**



4-isopropyloctane
or
4-(1-methylethyl)octane



6-(1,2-dimethylpropyl)-4-propyldecane

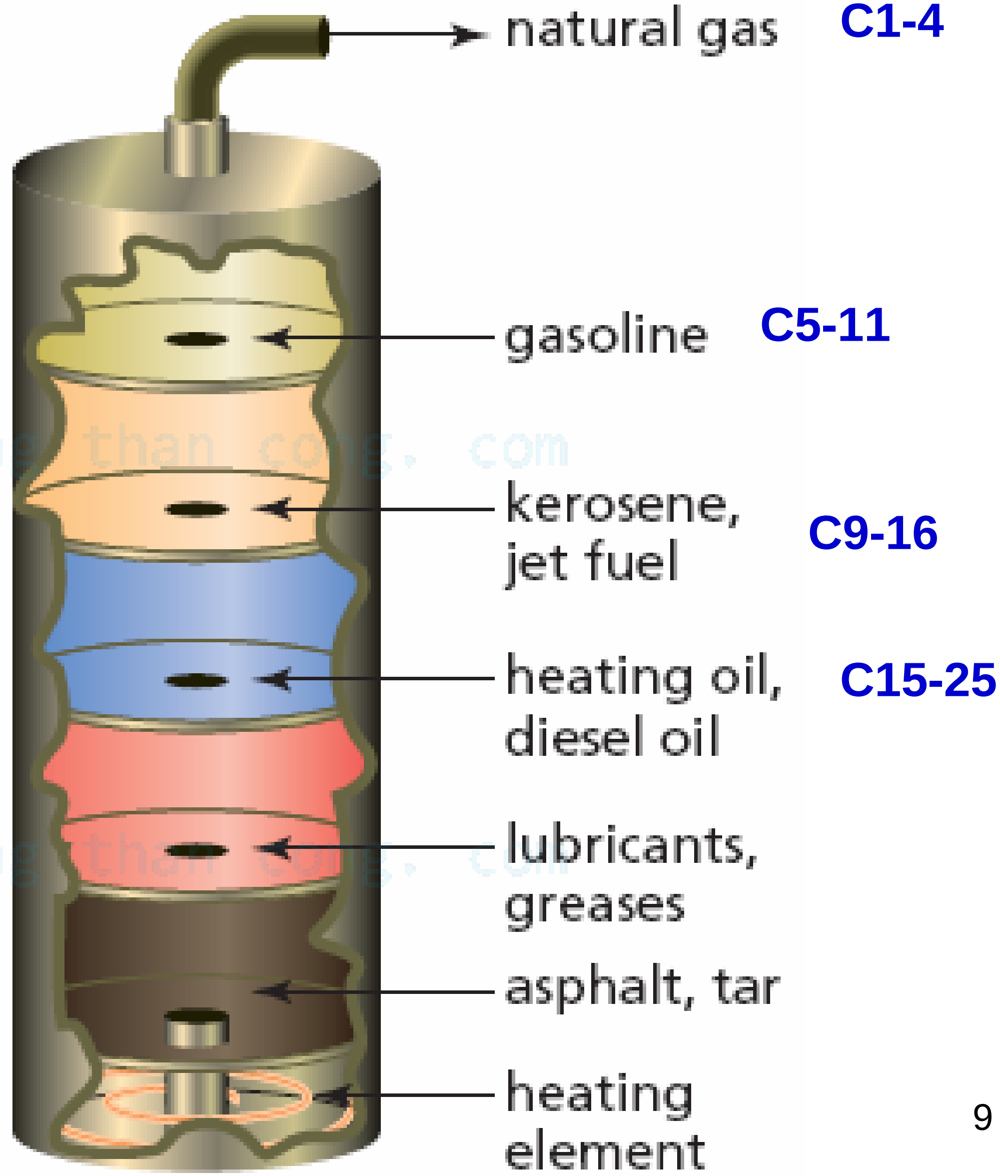


2,3-dimethyl-5-(2-methylbutyl)decane

NATURAL SOURCES OF ALKANES

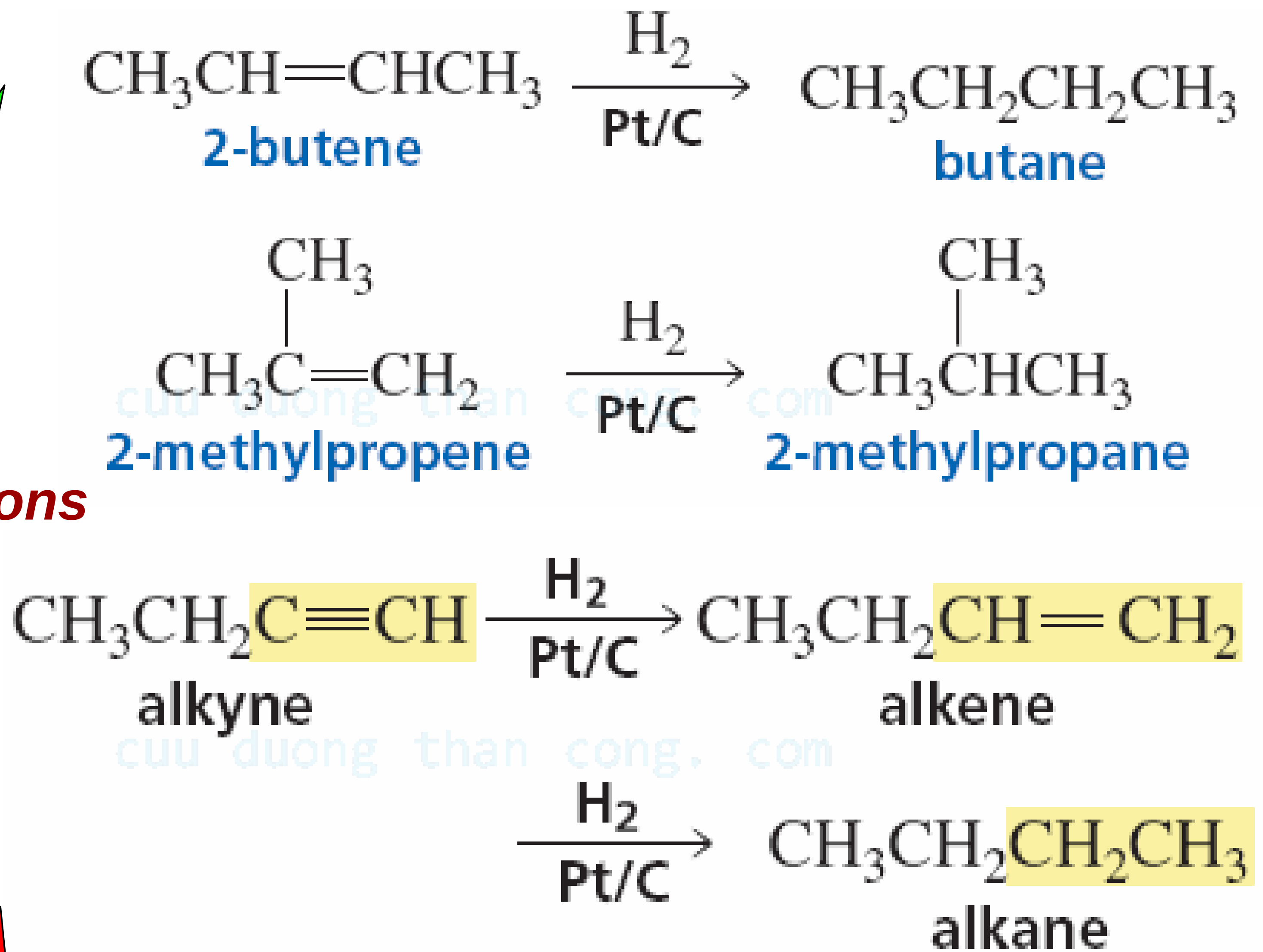
Natural gas &
petroleum

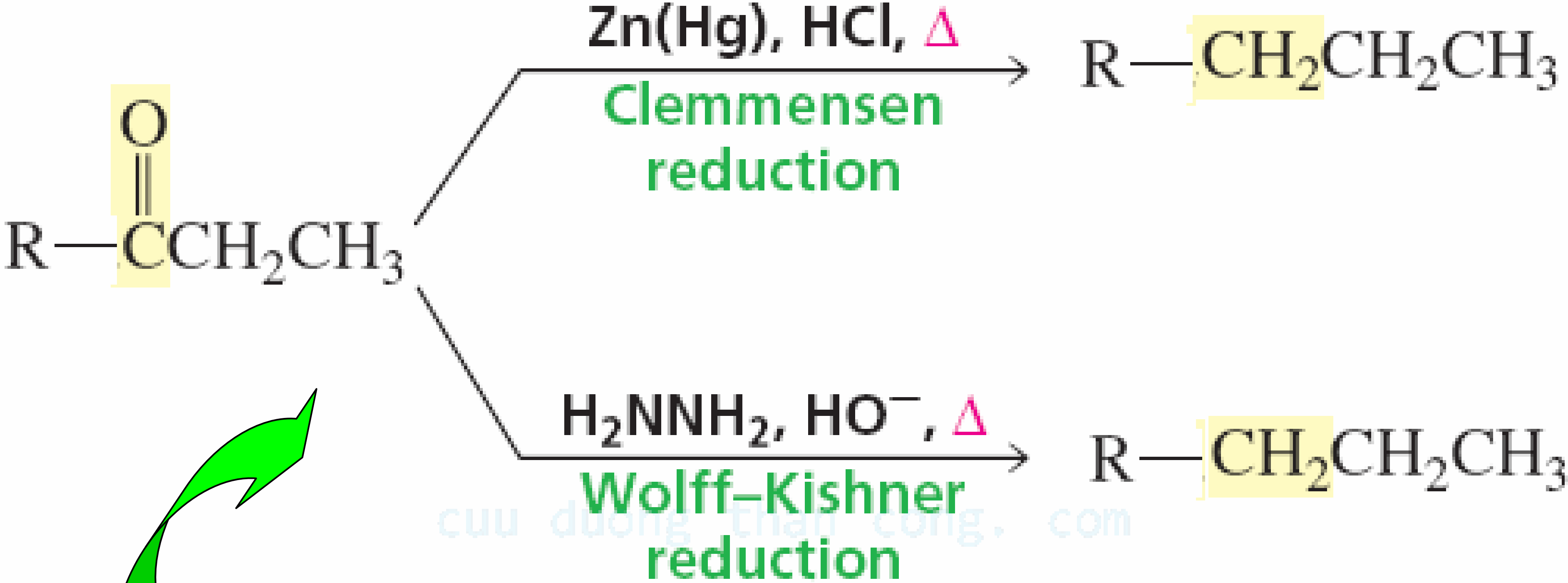
(fossil fuels)



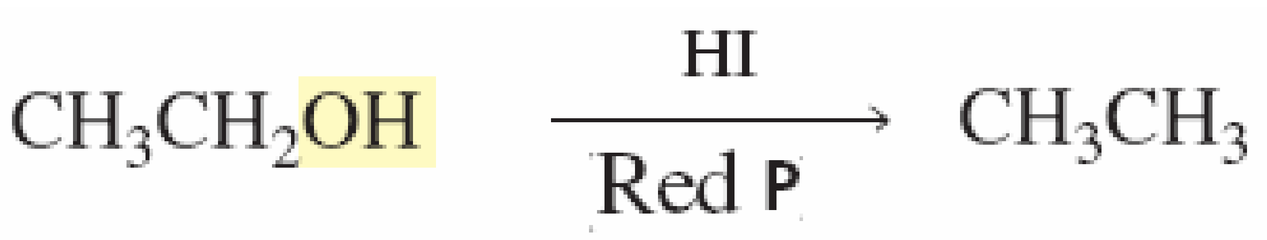
PREPARATION OF ALKANES

Catalytic hydrogenations of alkenes / alkynes





Reduction reactions



Wurtz reactions

symmetric alkane

$$CH_3CH_2CH_2Br + BrCH_2CH_2CH_3 \xrightarrow{Na} CH_3CH_2CH_2CH_2CH_2CH_3$$

Limitations:

+ The Wurtz reaction is limited to the synthesis of symmetric alkanes from alkyl iodides & bromides

+ If two dissimilar alkyl halides are taken as reactants, then the product is a mixture of alkanes that is, often, *difficult to separate*

+ A side reaction also occurs to produce an alkene

+ The side reaction becomes more significant when the alkyl halides are <u>bulky</u> at the halogen-attached carbon

Corey-House synthesis – the reaction of a lithium dialkyl cuprate with an alkyl halide to form a new alkane

$$CH_3CH_2CH_2Br \xrightarrow[\text{hexane}]{\text{Li}} CH_3CH_2CH_2Li$$

organolithium reagent

$$\xrightarrow[\text{THF}]{\text{CuI}} (CH_3CH_2CH_2)_2CuLi$$

Gilman reagent

$$CH_3CH_2CH_2CH_2Br + (CH_2CH_2CH_2)_2CuLi \xrightarrow{\text{THF}} CH_3CH_2CH_2CH_2CH_2CH_2CH_3$$

heptane

cuu duong than cong. com

Corey-House synthesis **overcomes some of the limitations of *the Wurtz reaction***

REACTIVITY OF ALKANES

- **Alkanes have only strong σ bonds**
- **Electronegativity of C & H are approximately the same**
- **None of the atoms in alkanes have any significant charge**
- **Neither nucleophiles nor electrophiles are attracted**

Alkanes are very unreactive

HALOGENATION OF ALKANES

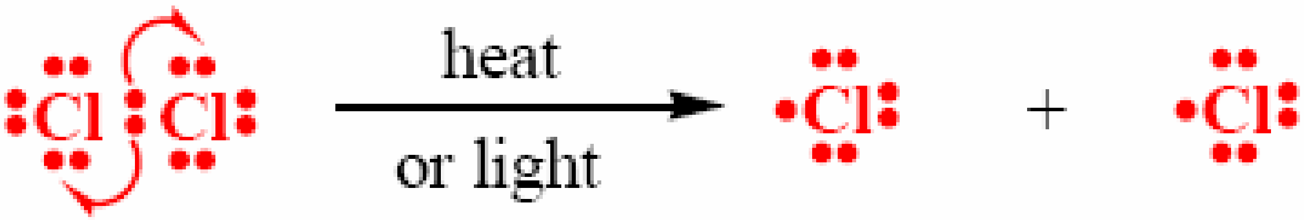
Radical Chlorination of Methane

Reaction:

$$CH_4 + Cl_2 \xrightarrow[\text{or light}]{\text{heat}} CH_3Cl + HCl$$

Mechanism:

Step 1 (**chain-initiating step – radicals are created**)

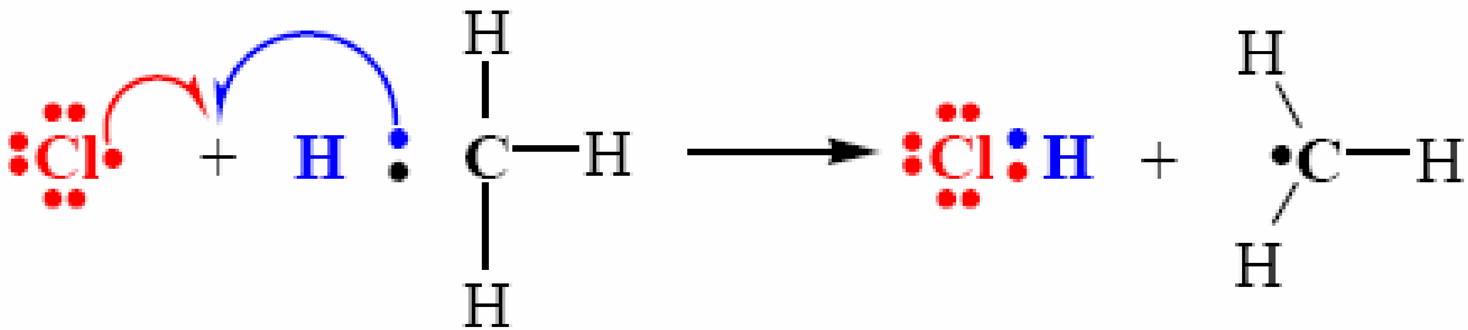


Under the influence of heat or light a molecule of chlorine dissociates; each atom takes one of the bonding electrons.

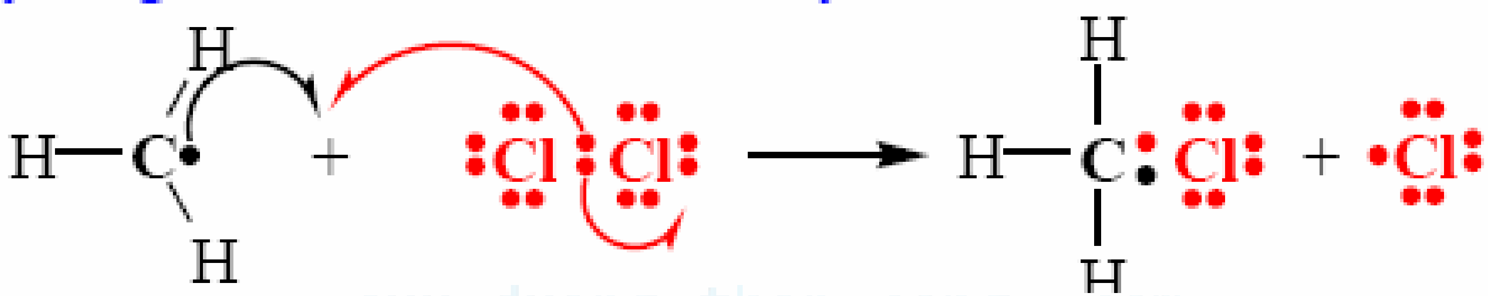
This step produces two highly reactive chlorine atoms.

Step 2

(chain-propagating step – one radical generates another)



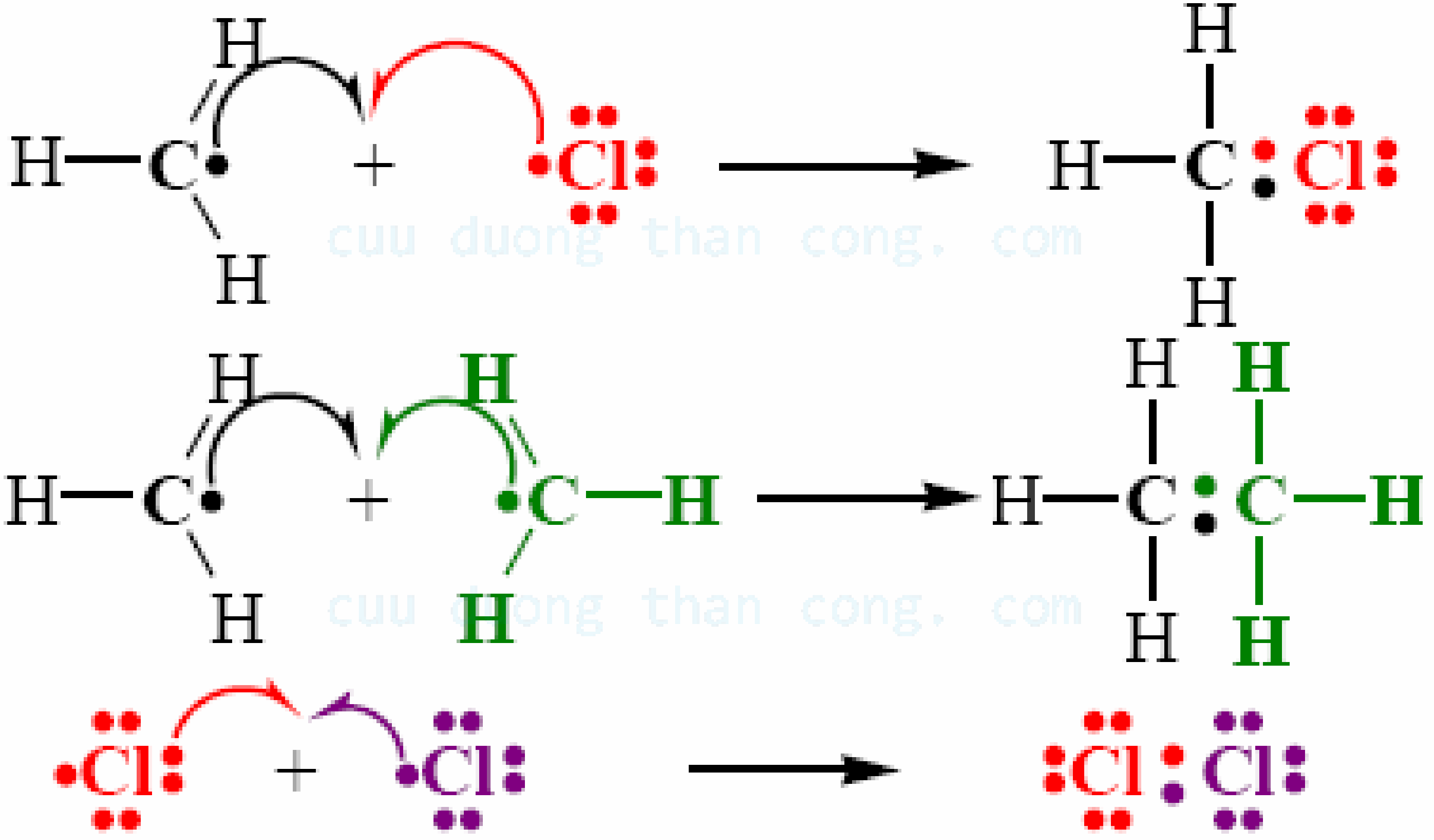
A chlorine atom abstracts a hydrogen atom from a methane molucule. This step produces a molecule of hydrogen chloride and a methyl radical.



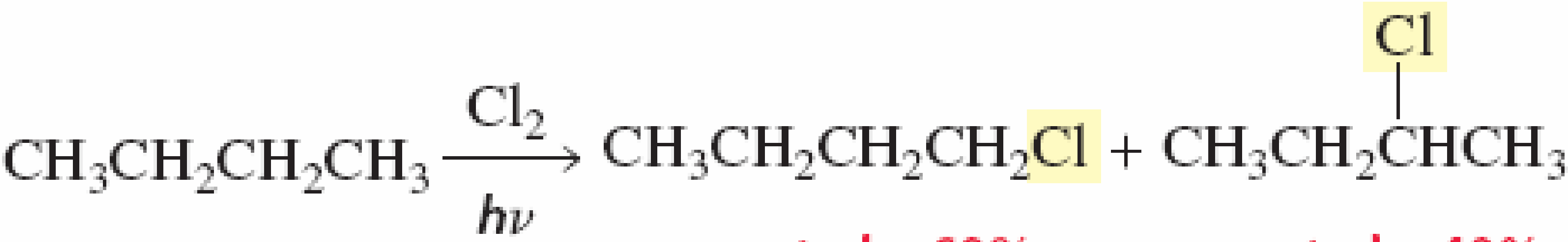
A methyl radical abstracts a chlorine atom from a chlorine molecule. This step produces a molecule of methyl chloride and a cholrine atom. The chlorine atom can now cause a repetition of Step 2.

Step 3

(**chain-terminating step — used up one or both radical intermediates**)

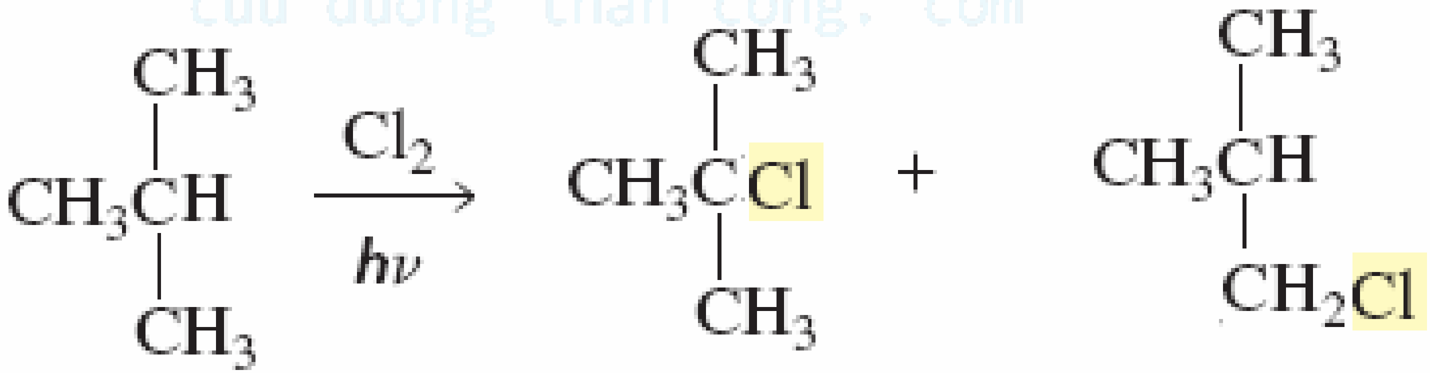


PRODUCT DISTRIBUTION



expected = 60%
experimental = 29%

expected = 40%
experimental = 71%



expected = 10%
experimental = 36%

expected = 90%
experimental = 64%

It must be easier to abstract a hydrogen atom from a secondary carbon than from a primary carbon

Reactivity - relative rate at which a particular hydrogen is abstracted in chlorination reactions:

tertiary > secondary > primary

5.0 3.8 1.0

At room temperature

← increasing rate of formation

↓

relative amount of 1-chlorobutane

number of hydrogens × reactivity

$6 \times 1.0 = 6.0$

$$\text{percent yield} = \frac{6.0}{21} = 29\%$$

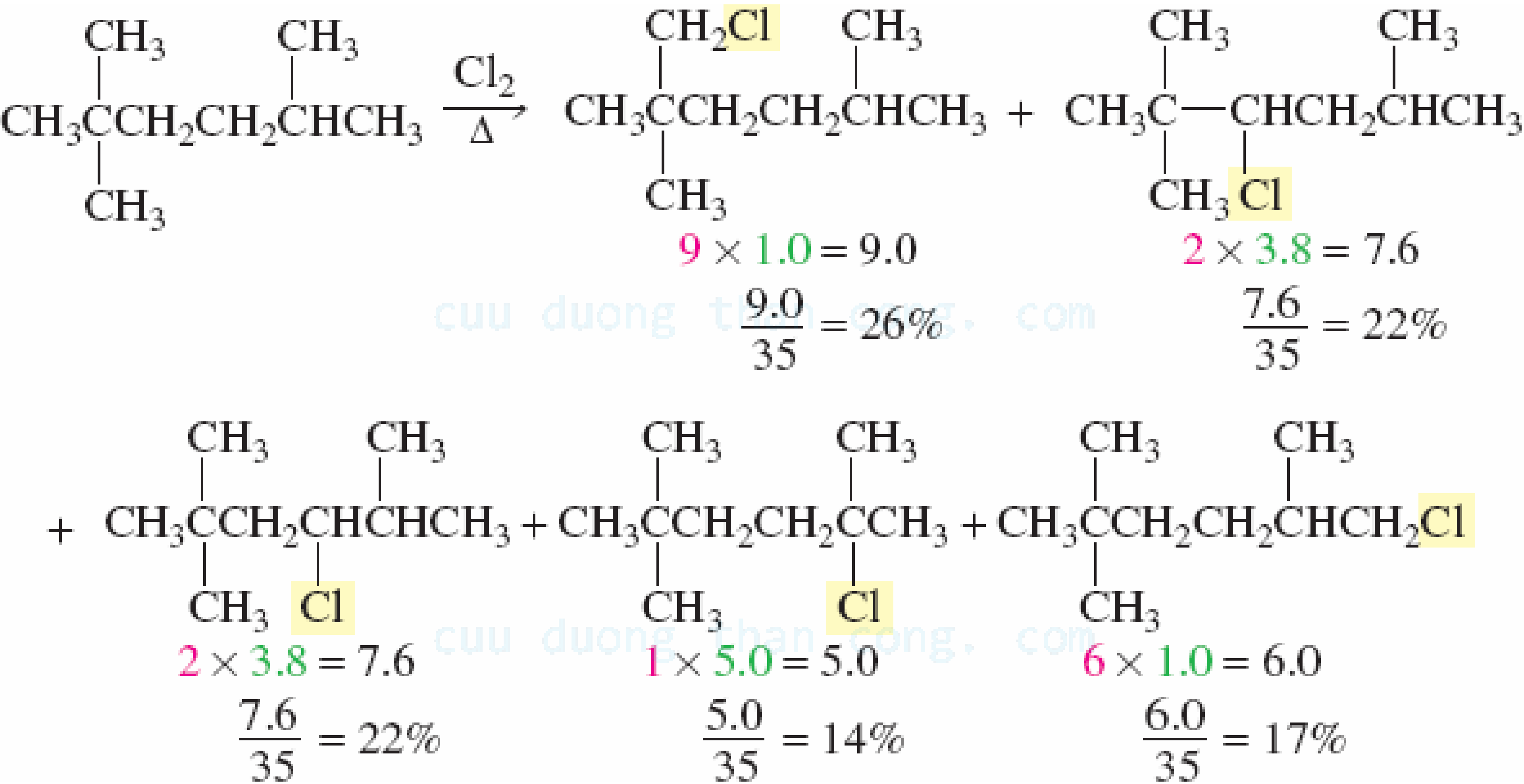
relative amount of 2-chlorobutane

number of hydrogens × reactivity

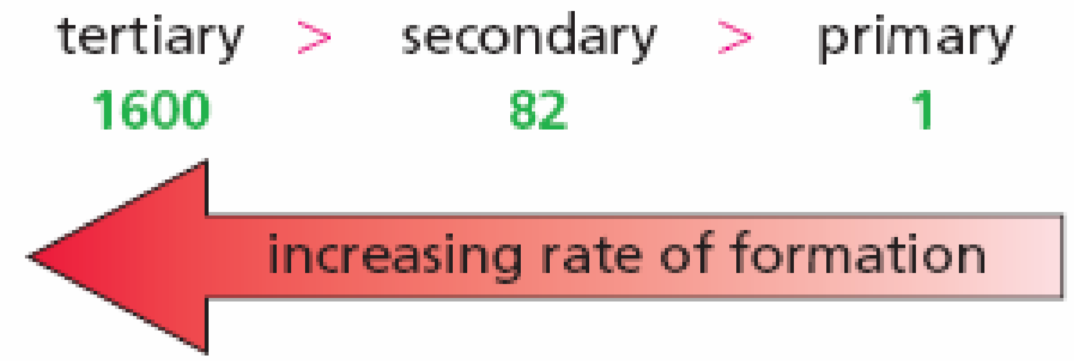
$4 \times 3.8 = 15$

$$\text{percent yield} = \frac{15}{21} = 71\%$$

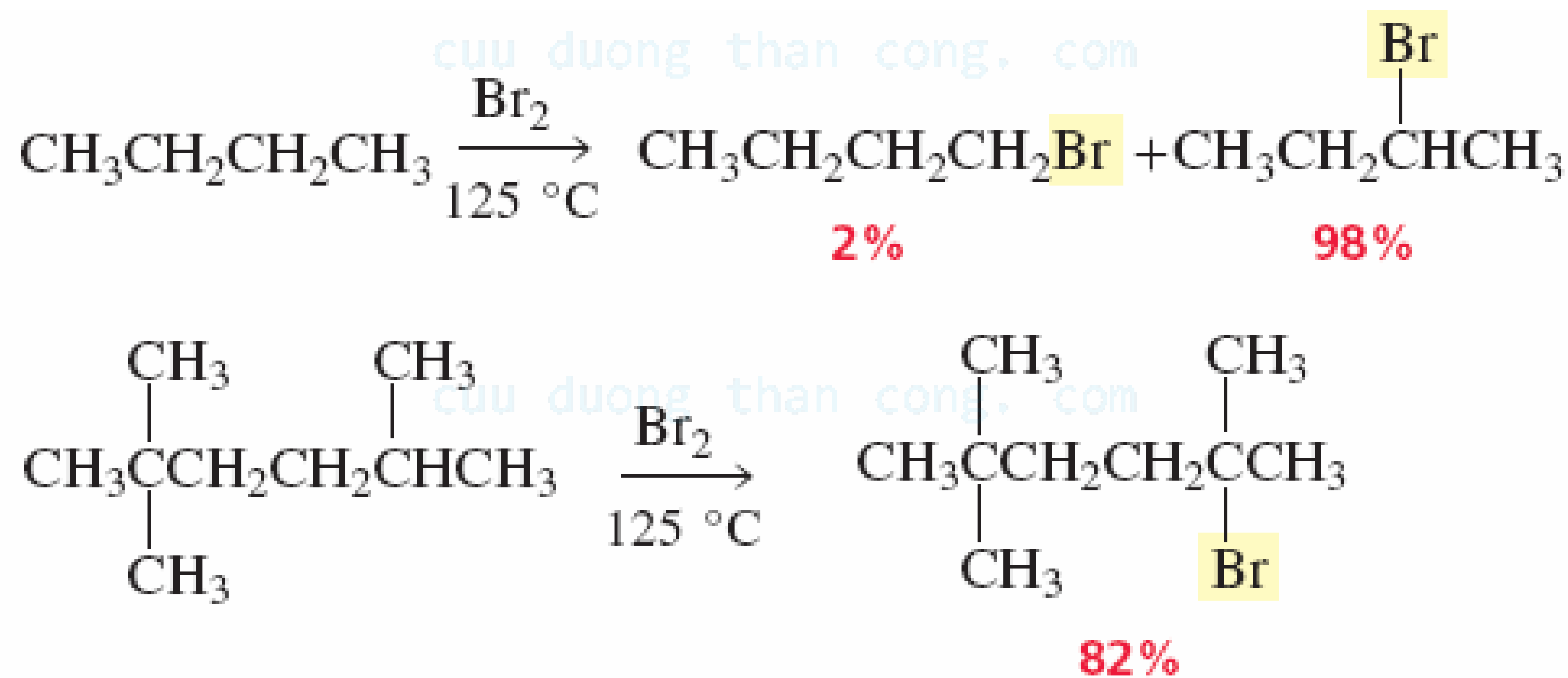
Product distribution can be estimated:



Br_2 *is less reactive* towards alkane than Cl_2, but Br_2 *is* ***more selective***



Bromination at 125 °C



$$F\cdot + CH_4 \longrightarrow \cdot CH_3 + HF \qquad 105 - 136 = -31$$
$$\cdot CH_3 + F_2 \longrightarrow CH_3F + F\cdot \qquad 38 - 108 = -70$$
$$\Delta H^\circ = -101 \text{ kcal/mol}$$

Too violent

$$Cl\cdot + CH_4 \longrightarrow \cdot CH_3 + HCl \qquad 105 - 103 = 2$$
$$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot \qquad 58 - 84 = -26$$
$$\Delta H^\circ = -24 \text{ kcal/mol}$$

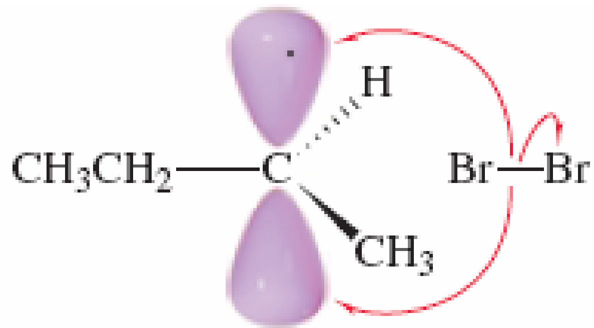
$$Br\cdot + CH_4 \longrightarrow \cdot CH_3 + HBr \qquad 105 - 87 = 18$$
$$\cdot CH_3 + Br_2 \longrightarrow CH_3Br + Br\cdot \qquad 46 - 70 = -24$$
$$\Delta H^\circ = -6 \text{ kcal/mol}$$

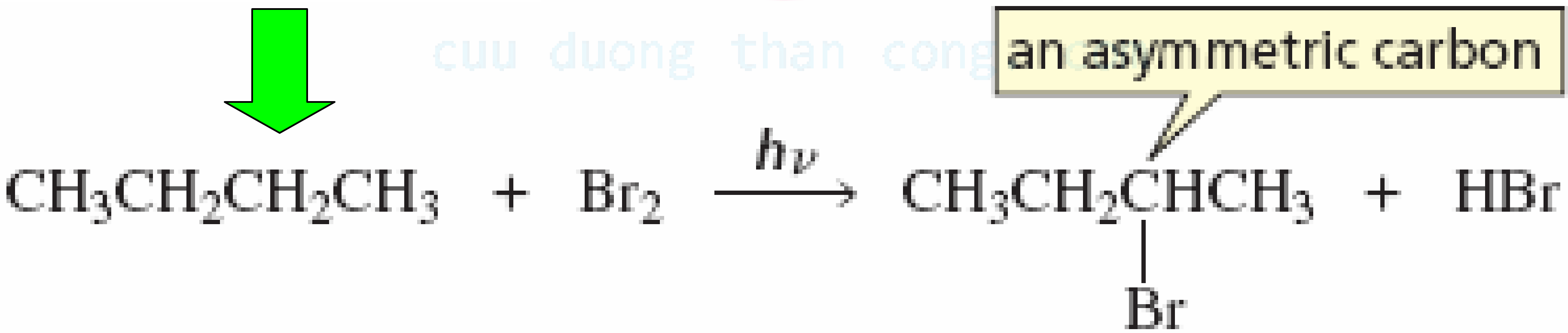
$$I\cdot + CH_4 \longrightarrow \cdot CH_3 + HI \qquad 105 - 71 = 34$$
$$\cdot CH_3 + I_2 \longrightarrow CH_3I + I\cdot \qquad 36 - 57 = -21$$
$$\Delta H^\circ = 13 \text{ kcal/mol}$$

Too slow

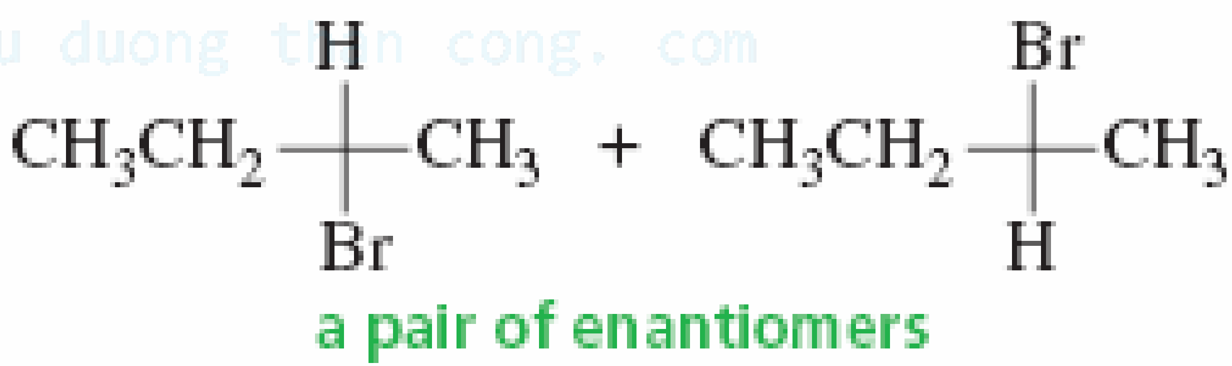
STEREOCHEMISTRY OF RADICAL SUBSTITUTION REACTIONS

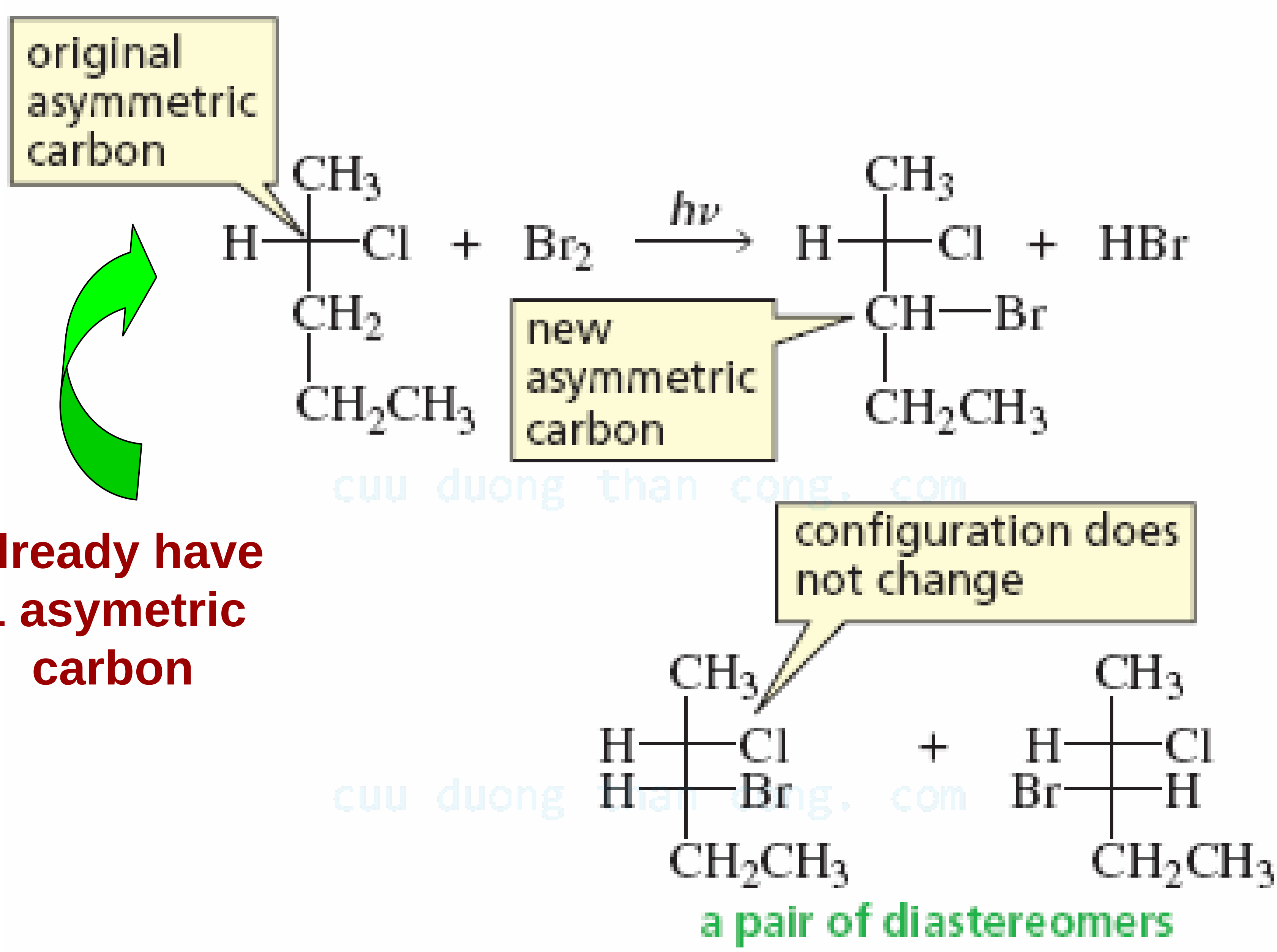
Have no asymetric carbon





Racemic mixture





Already have 1 asymetric carbon

COMBUSTION OF ALKANES

Heats of Combustion ($-\Delta H^\circ$) of Representative Alkanes

Compound	Formula	$-\Delta H^\circ$ kJ/mol	$-\Delta H^\circ$ kcal/mol
Unbranched alkanes			
Hexane	$CH_3(CH_2)_4CH_3$	4,163	995.0
Heptane	$CH_3(CH_2)_5CH_3$	4,817	1151.3
Octane	$CH_3(CH_2)_6CH_3$	5,471	1307.5
Nonane	$CH_3(CH_2)_7CH_3$	6,125	1463.9
Decane	$CH_3(CH_2)_8CH_3$	6,778	1620.1
Undecane	$CH_3(CH_2)_9CH_3$	7,431	1776.1
Dodecane	$CH_3(CH_2)_{10}CH_3$	8,086	1932.7
Hexadecane	$CH_3(CH_2)_{14}CH_3$	10,701	2557.6
2-Methyl-branched alkanes			
2-Methylpentane	$(CH_3)_2CHCH_2CH_2CH_3$	4,157	993.6
2-Methylhexane	$(CH_3)_2CH(CH_2)_3CH_3$	4,812	1150.0
2-Methylheptane	$(CH_3)_2CH(CH_2)_4CH_3$	5,466	1306.3