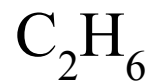
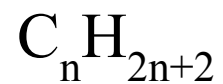


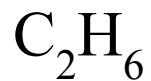
Alkanes

ALKANES

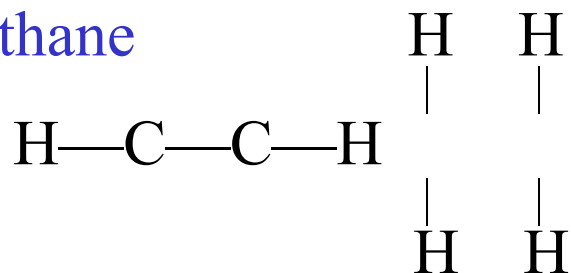
(a “family” of hydrocarbons)



etc.

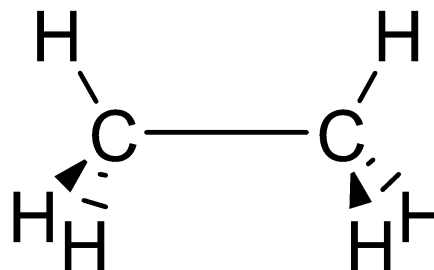


ethane



sp^3 , bond angles = 109.5°

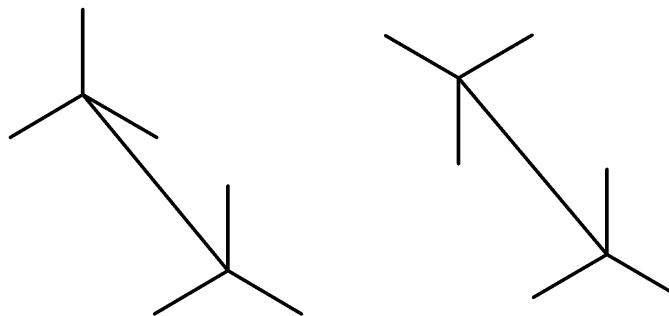
σ -bonds (sigma)

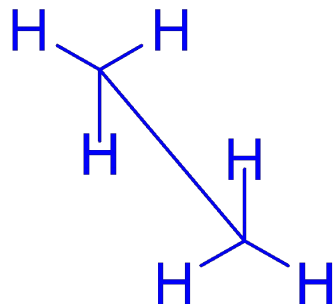


rotation about C--C (**conformations**)

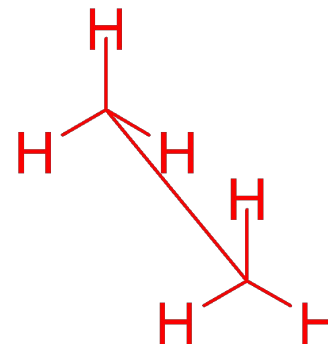
representation:

“andiron” or “sawhorse”





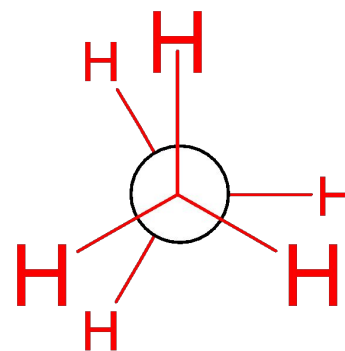
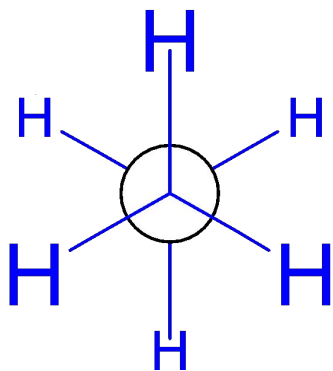
“staggered”

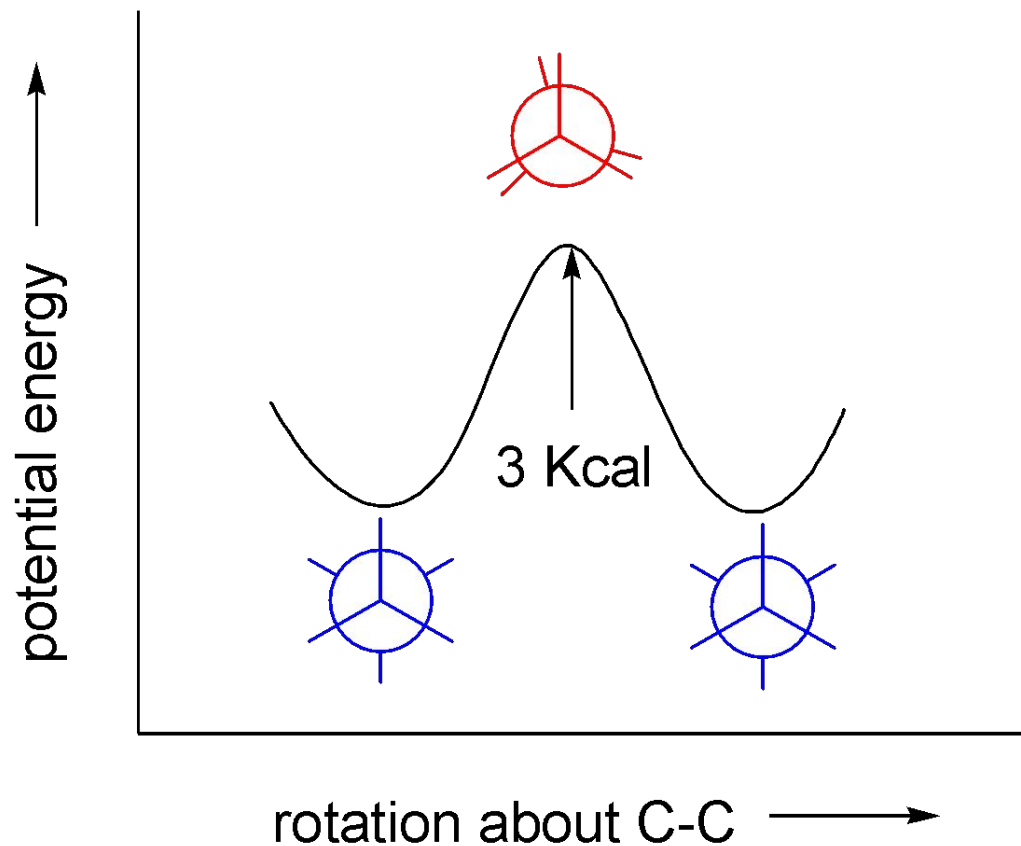


“eclipsed”

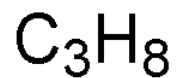
torsional strain: deviation from staggered.

Newman projections:

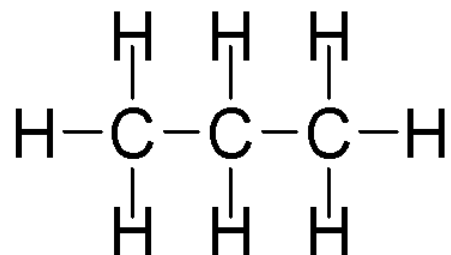




The barrier to rotation about the carbon-carbon bond in ethane is 3 Kcal/mole. The rotation is ~ “free.”



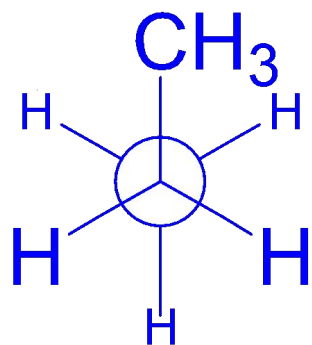
propane



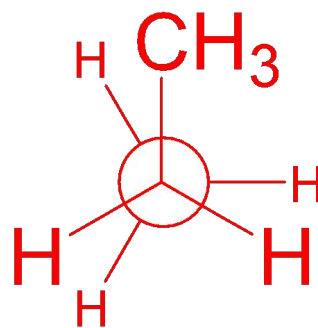
projection formula



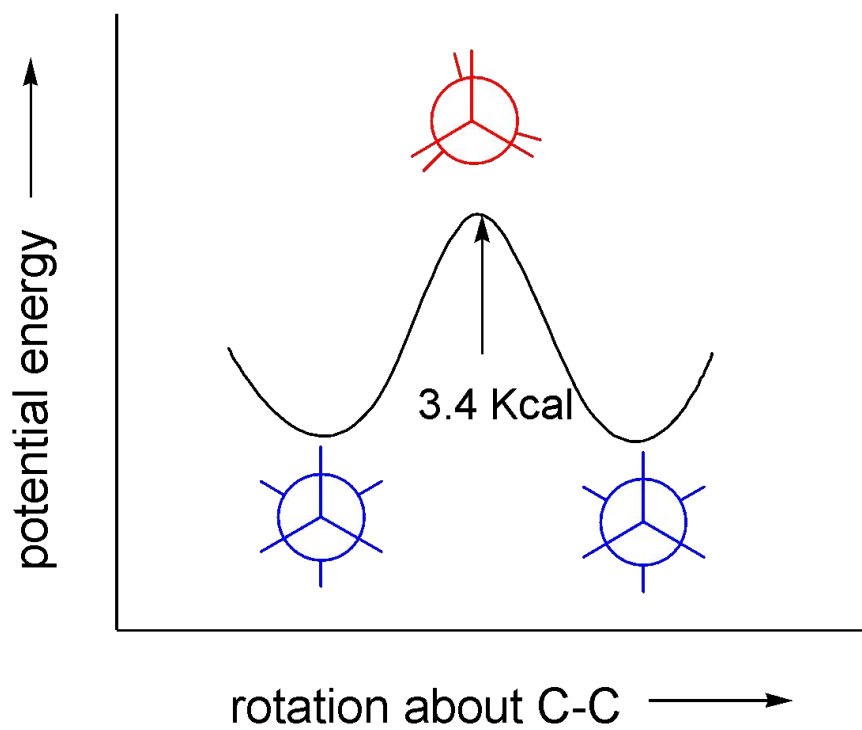
partially condensed formula



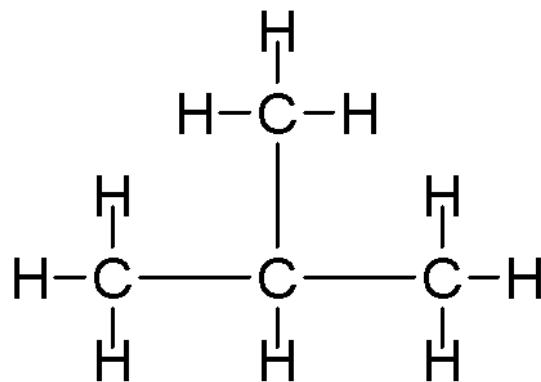
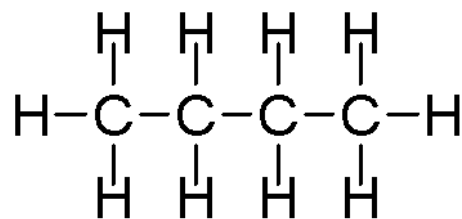
staggered



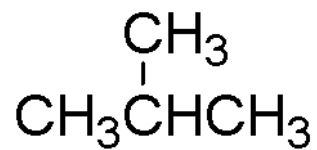
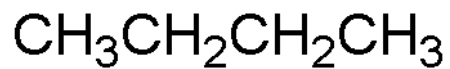
eclipsed



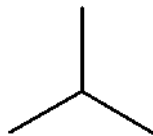
C_4H_{10} butane(s)



projection



partially condensed



stick formulas

Two isomers of butane C_4H_{10} :



bp 0 °C

mp -138 °C

d 0.622 g/cc

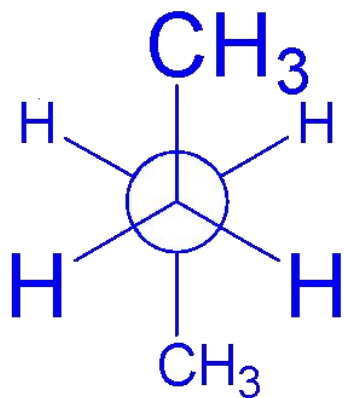


bp -12 °C

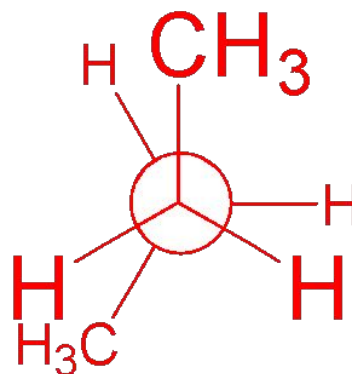
mp -159 °C

d 0.604 g/cc

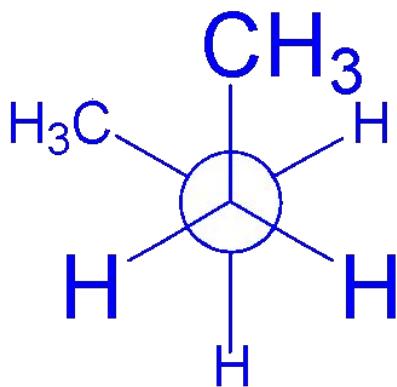
Conformations about C2-C3 in *n*-butane:



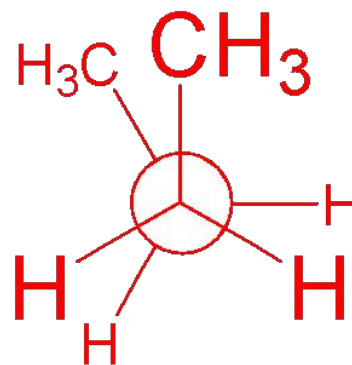
anti



CH₃/H eclipsed

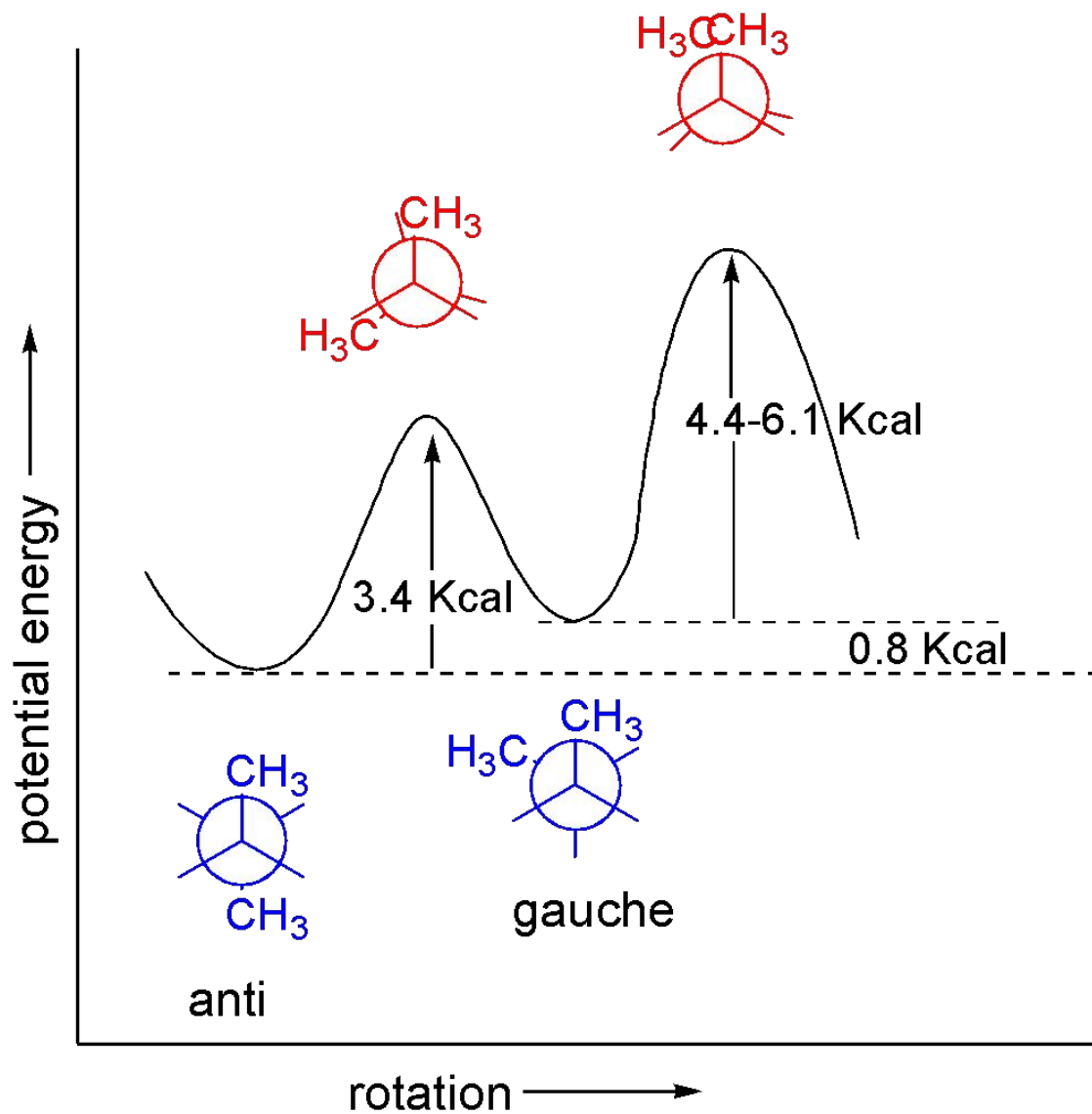


gauche



CH₃/CH₃ eclipsed

conformations about C2-C3 in *n*-butane:

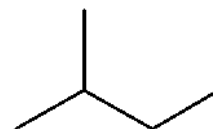


C_5H_{12} pentane(s)

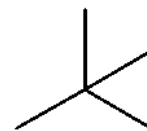
$CH_3CH_2CH_2CH_2CH_3$ *n*-pentane



$\begin{array}{c} CH_3 \\ | \\ CH_3CHCH_2CH_3 \end{array}$ isopentane



$\begin{array}{c} CH_3 \\ | \\ CH_3CCH_3 \\ | \\ CH_3 \end{array}$ neopentane

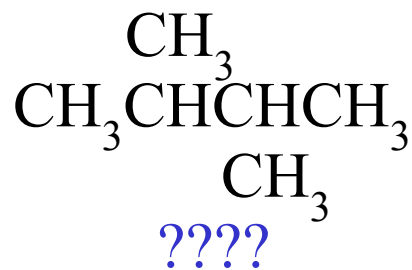
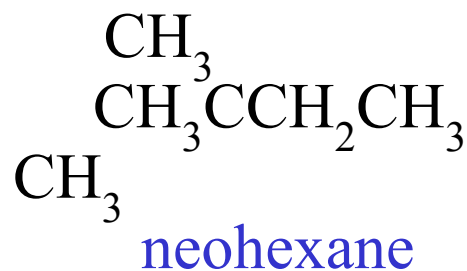
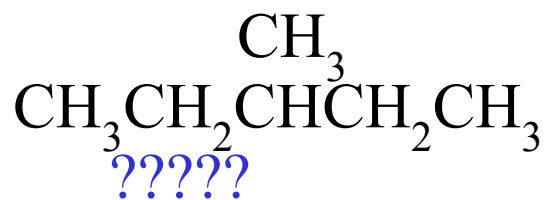
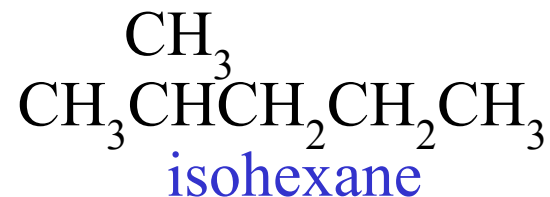


these are common, or trivial, names where a prefix is used to indicate the structure.

Alkane	name	isomers
CH_4	methane	1
C_2H_6	ethane	1
C_3H_8	propane	1
C_4H_{10}	butanes	2
C_5H_{12}	pentanes	3
C_6H_{14}	hexanes	5
C_7H_{16}	heptanes	9
C_8H_{18}	octanes	18
C_9H_{20}	nonanes	35
$\text{C}_{10}\text{H}_{22}$	decane	75
.....		
$\text{C}_{20}\text{H}_{42}$	eicosane	366,319

each new **common**
name requires a new
prefix...

hexanes C_6H_{14} common names



IUPAC nomenclature (Geneva, 1920)

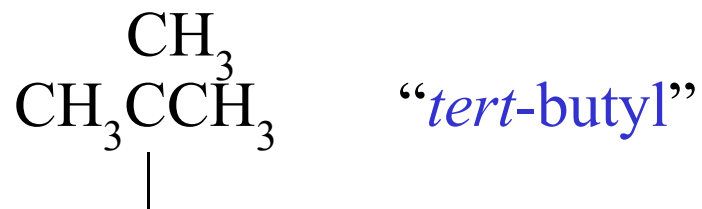
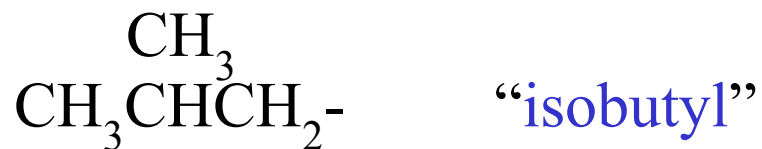
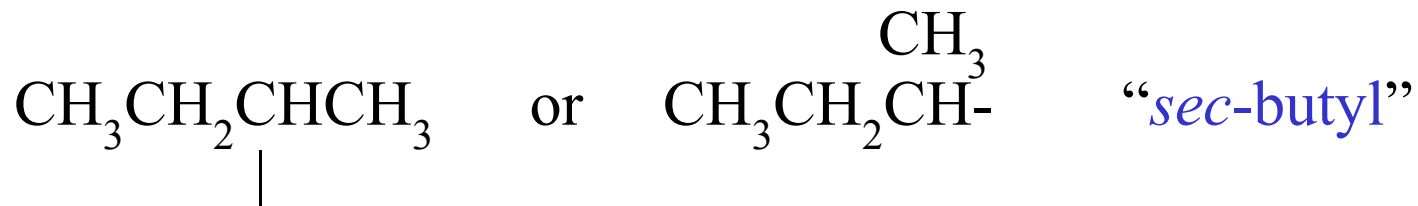
names of radicals (alkyl groups):

CH_3 - “methyl” CH_3Cl methyl chloride

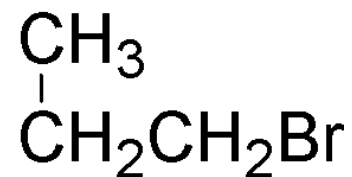
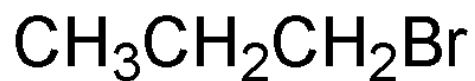
CH_3OH methyl alcohol, etc.

CH_3CH_2 - “ethyl”

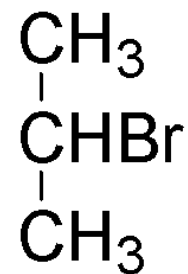
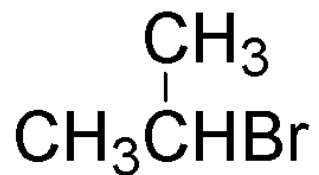
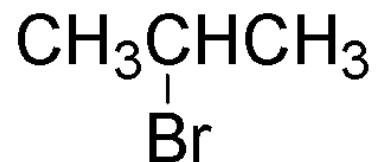
$\text{CH}_3\text{CH}_2\text{CH}_2$ - “*n*-propyl” $\text{CH}_3\text{CH}(\text{CH}_3)_2$ “isopropyl”



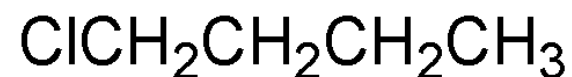
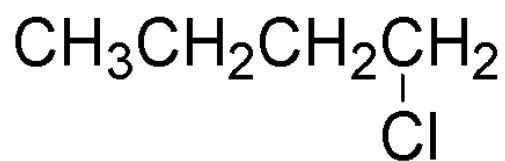
n-propyl bromide



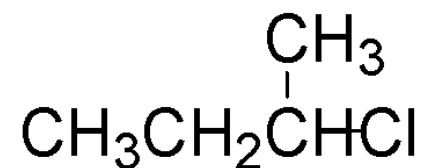
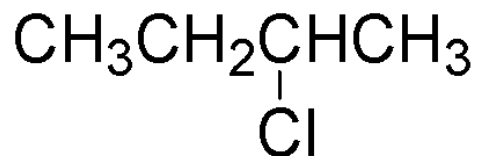
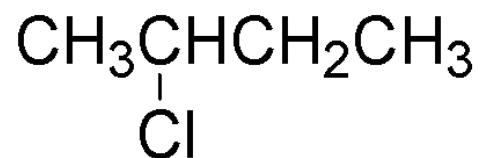
isopropyl bromide



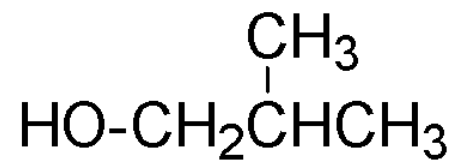
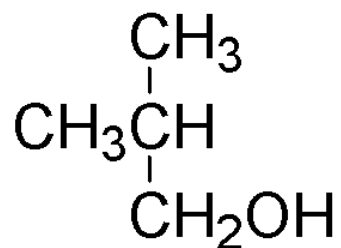
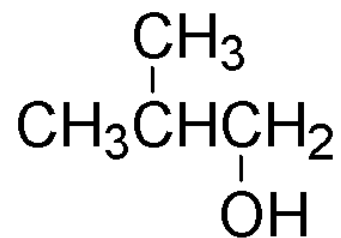
n-butyl chloride



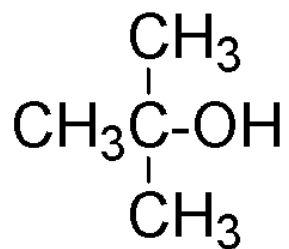
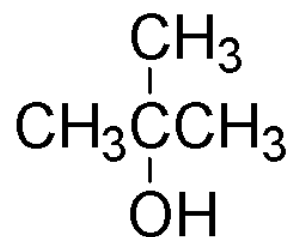
sec-butyl chloride



isobutyl alcohol



tert-butyl alcohol



Web problems to help with naming and recognizing organic radicals:

[Click here](#)

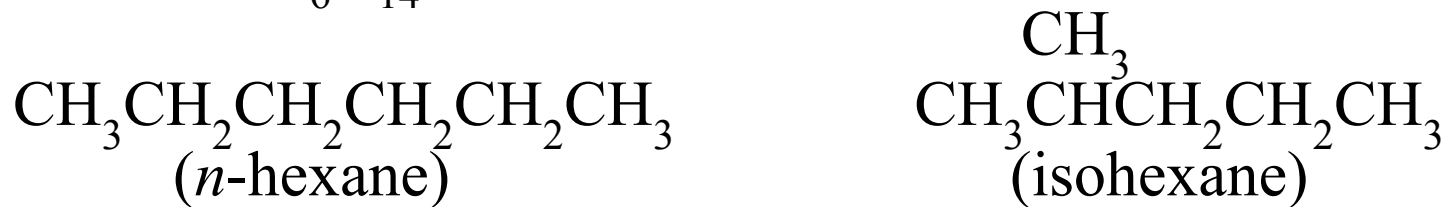
or copy and paste on the address line in your browser:

<http://proton.csudh.edu/structures/butyls/hwbutyls.html>

IUPAC rules for naming alkanes:

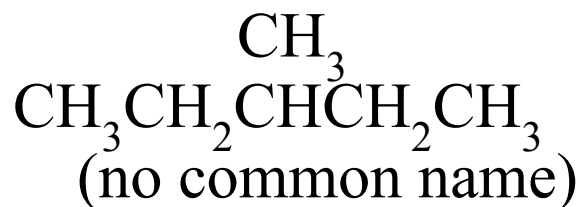
1. parent chain = longest continuous carbon chain □ “alkane”.
2. branches on the parent chain are named as “alkyl” groups.
3. number the parent chain starting from the end that gives you the lower number for the first branch (principle of lower number).
4. assign “locants” to the alkyl branches.
5. if an alkyl group appears more than once use prefixes: di, tri, tetra, penta...; each alkyl group must have a locant!
6. the name is written as one word with the parent name last. The names and locants for the alkyl branches are put in alphabetic order (ignore all prefixes except iso) separating numbers from numbers with commas and letters from numbers with hyphens.

hexanes C_6H_{14} IUPAC names

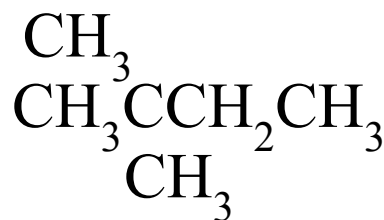


n-hexane

2-methylpentane

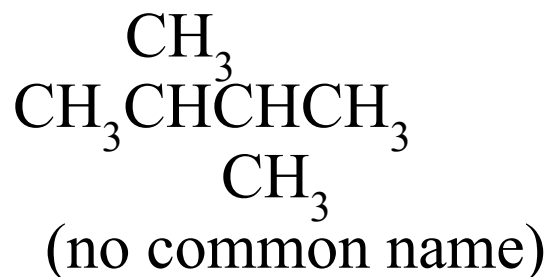


3-methylpentane

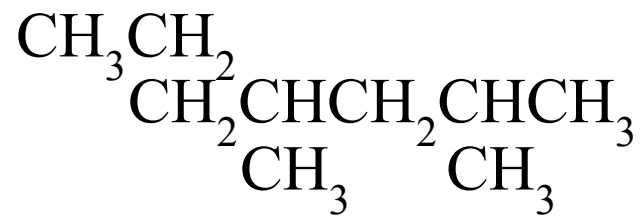


(neohexane)

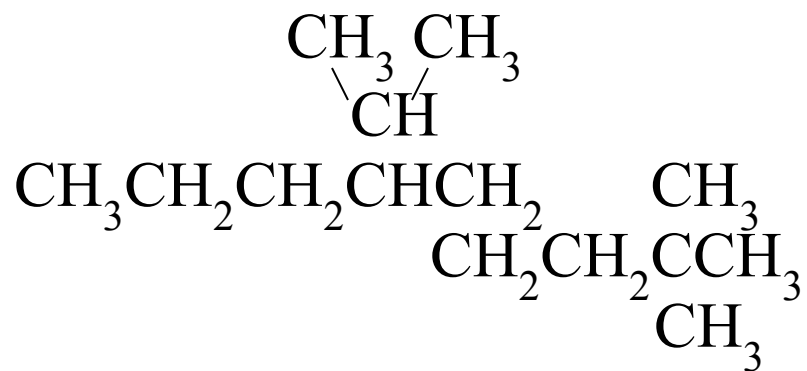
2,2-dimethylbutane



2,3-dimethylbutane



2,4-dimethylheptane



6-isopropyl-2,2-dimethylnonane

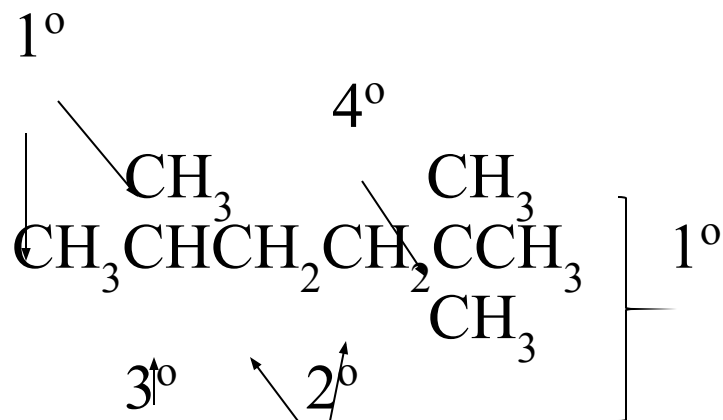
“**classes** of carbons”

primary carbon (1°) – a carbon bonded to one carbon

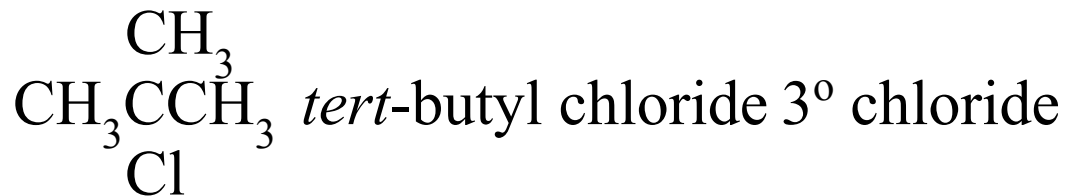
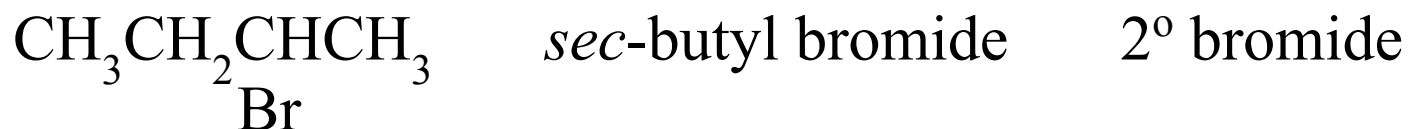
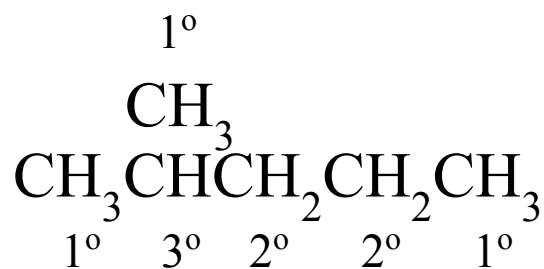
secondary carbon (2°) – a carbon bonded to two carbons

tertiary carbon (3°) – a carbon bonded to three carbons

quaternary carbon (4°) – a carbon bonded to four carbons



classification of hydrogens, halides – hydrogens or halides are classified by the carbon to which they are attached.



alkanes, **physical properties**

non-polar or only weakly polar, cannot hydrogen bond □
relatively weak intermolecular forces

lower mp/bp; increase with size; decrease with branching

@ room temperature:

$C_1 - C_4$ are gases

$C_5 - C_{17}$ are liquids

$> C_{17}$ are solids

alkanes are water insoluble

<u>alkane</u>	<u>mp °C</u>	<u>bp °C</u>
methane	-183	-162
ethane	-172	-89
propane	-187	-42
<i>n</i> -butane	-138	0
<i>n</i> -pentane	-130	36
<i>n</i> -hexane	-95	69
...		
<i>n</i> -heptadecane	22	292
<i>n</i> -octadecane	28	308

branching lowers mp/bp

<i>n</i> -pentane	-130	36
isopentane	-160	28

fossil fuels:

natural gas

petroleum

coal

petroleum is a complex mixture of hydrocarbons

1. solvents

2. fuels

3. raw materials for chemical syntheses

separated into fractions by fractional distillation in an oil refinery

products from fractional distillation of petroleum:

fraction	b. range	carbons
natural gas	below 20°	C ₁ – C ₄
petroleum “ether”	20 – 60°	C ₅ – C ₆
ligroin	60 – 100°	C ₆ – C ₇
raw gasoline	40 – 205°	C ₅ – C ₁₀
kerosine	175 – 325°	C ₁₂ – C ₁₈
gas oil	above 275°	C ₁₂ & up
lube oil	non-volatile liquids	
asphalt	non-volatile solids	
coke	solid carbon	

syntheses

Industrial

large amounts (tons)

lowest cost

mixtures often okay

dedicated apparatus

Laboratory

small amounts (grams)

non-profit

pure substances

flexible apparatus

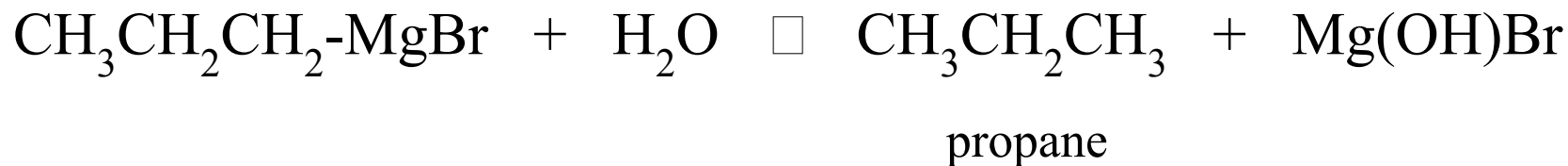
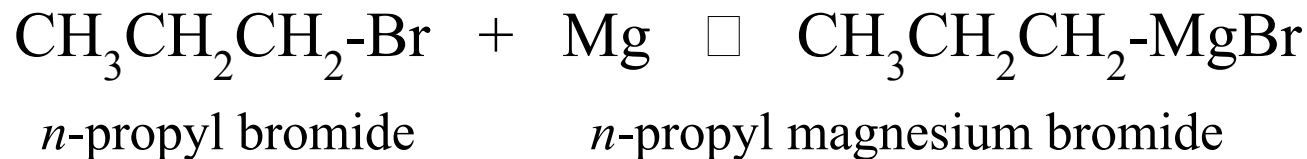
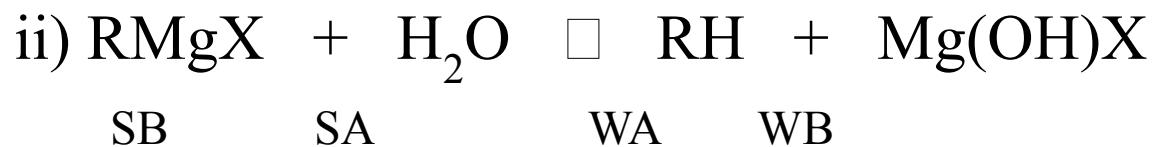
on exams, homework: laboratory syntheses!

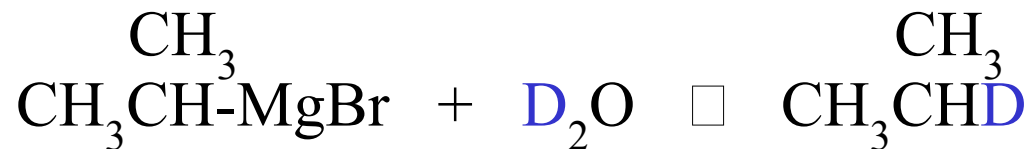
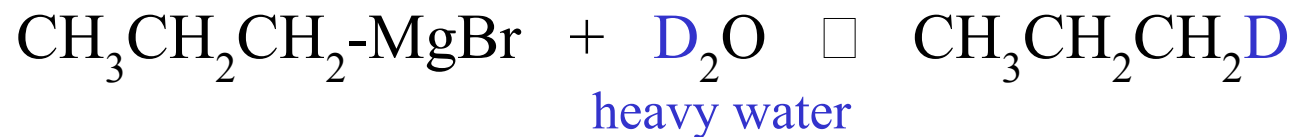
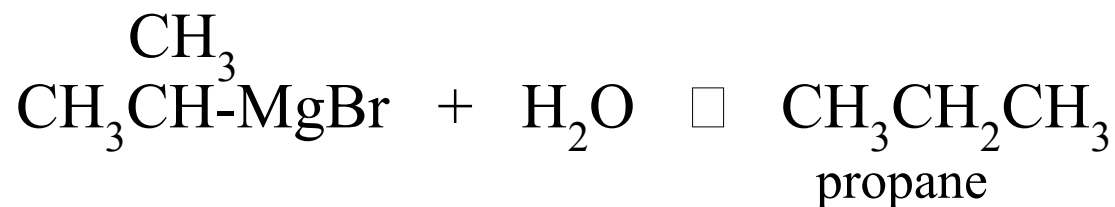
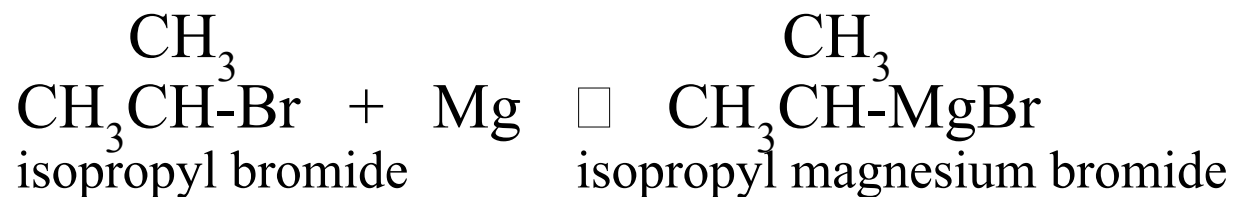
Alkanes, syntheses:

1. (to be covered later)
2. Reduction of an alkyl halide
 - a) hydrolysis of a Grignard reagent
 - b) with an active metal and an acid
3. Corey-House synthesis
(coupling of an alkyl halide with lithium dialkylcopper)

2. Reduction of an alkyl halide

a) hydrolysis of a Grignard reagent (two steps)



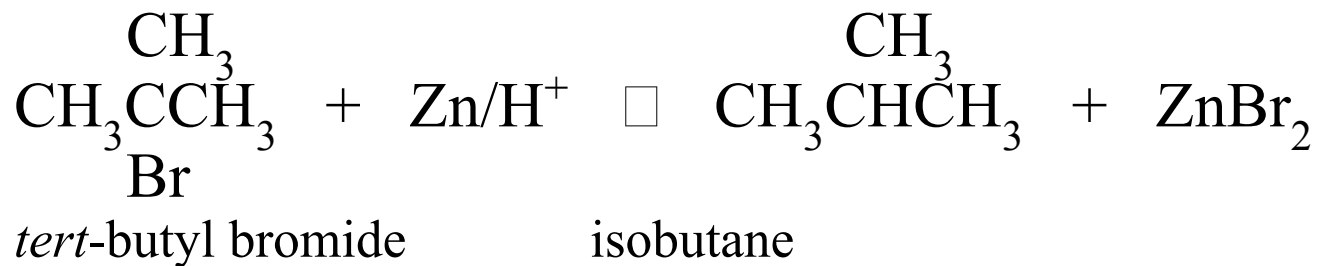
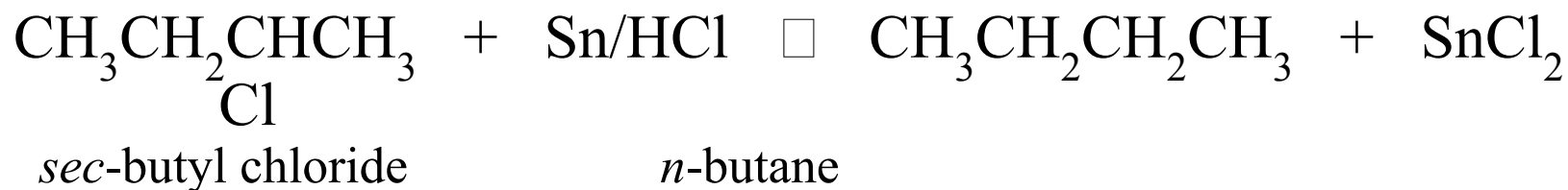


b) with an active metal and an acid

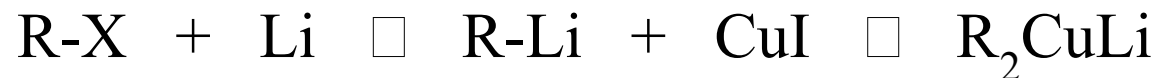


active metals = Sn, Zn, Fe, etc.

acid = HCl, etc. (H^+)



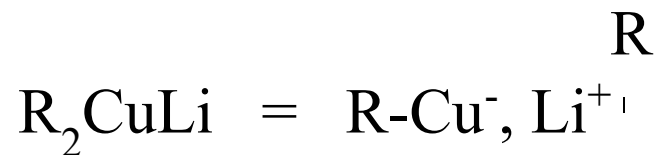
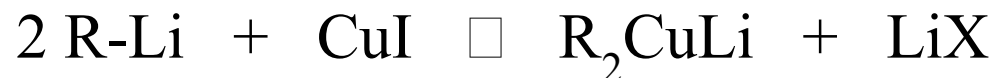
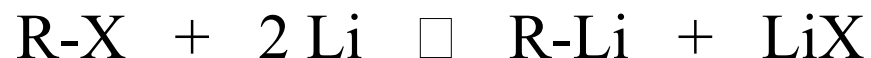
3. Corey-House synthesis

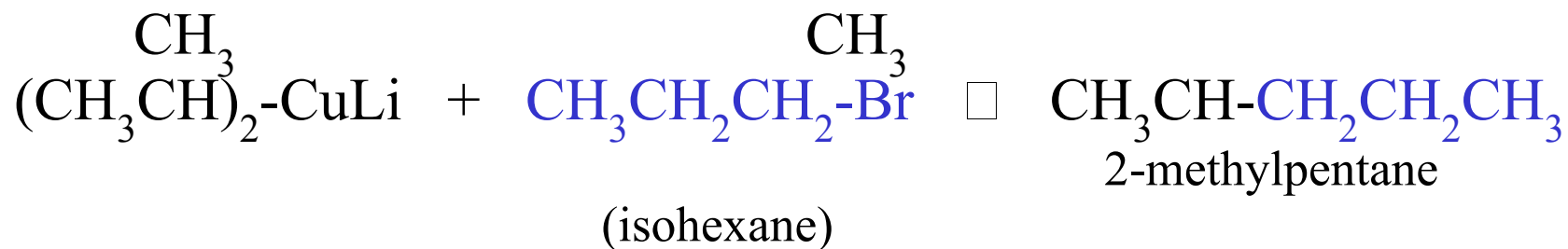


(R'-X should be 1° or methyl)

This synthesis is important because it affords a synthesis of a larger alkane from two smaller alkyl halides.

note: the previous equations are not balanced:

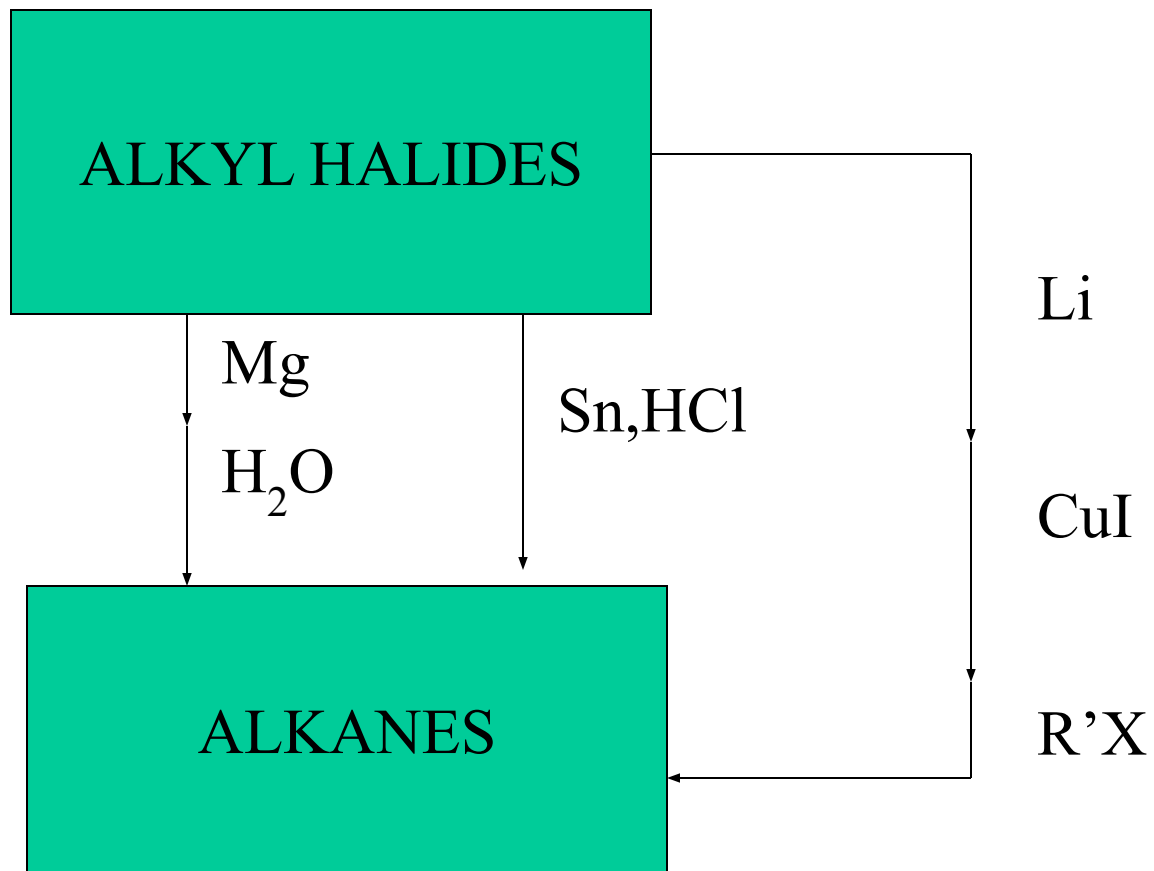




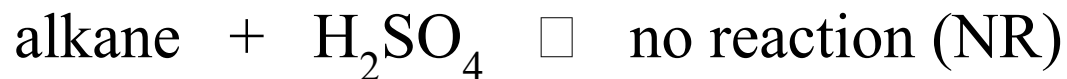
Note: the R'X should be a 1° or methyl halide for the best yields of the final product.

Alkanes, syntheses:

1. (to be covered later)
2. Reduction of an alkyl halide
 - a) hydrolysis of a Grignard reagent
 - b) with an active metal and an acid
3. Corey-House synthesis
(coupling of an alkyl halide with lithium dialkylcopper)



Reactions of alkanes:

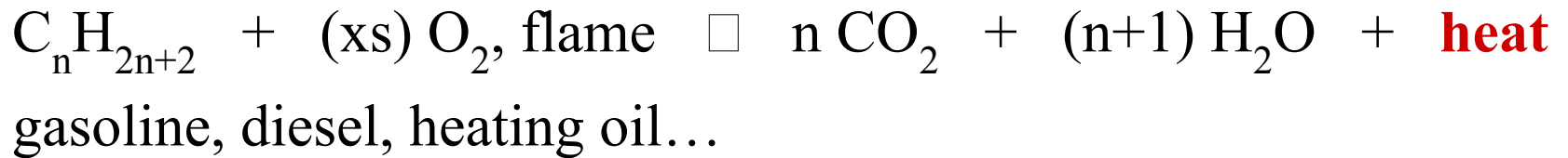


(Alkanes are typically non-reactive. They don't react with acids, bases, active metals, oxidizing agents, reducing agents, halogens, etc.)

Alkane, reactions:

1. Halogenation
2. Combustion (oxidation)
3. Pyrolysis (cracking)

2. Combustion

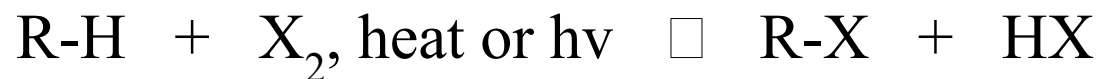


3. Pyrolysis (cracking)



Used to increase the yield of gasoline from petroleum. Higher boiling fractions are “cracked” into lower boiling fractions that are added to the raw gasoline. The alkenes can be separated and used in to make plastics.

1. Halogenation



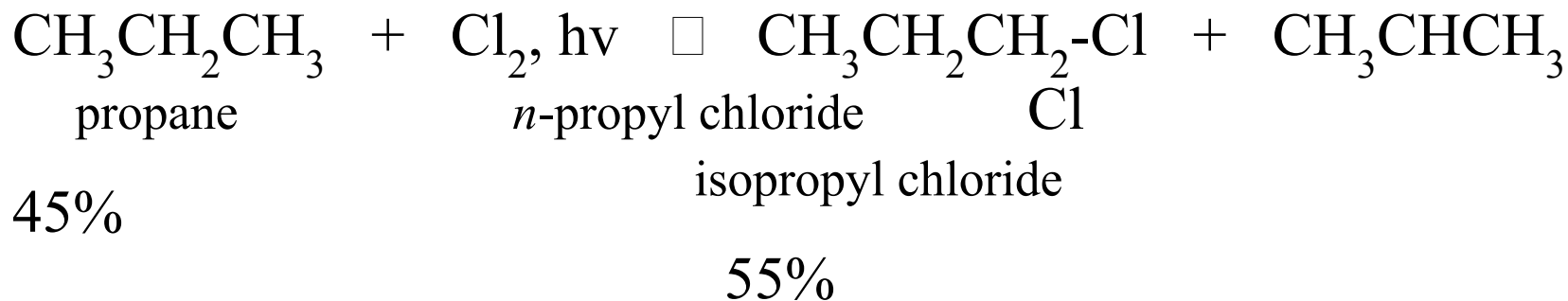
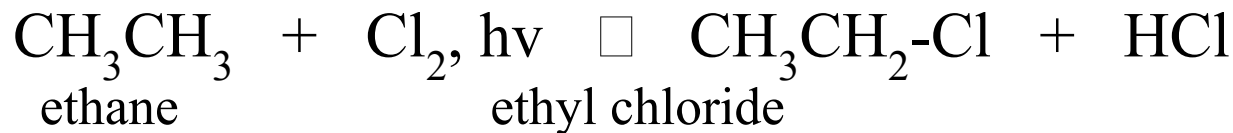
a) heat or light required for reaction.

b) X_2 : $\text{Cl}_2 > \text{Br}_2 \neq \text{I}_2$

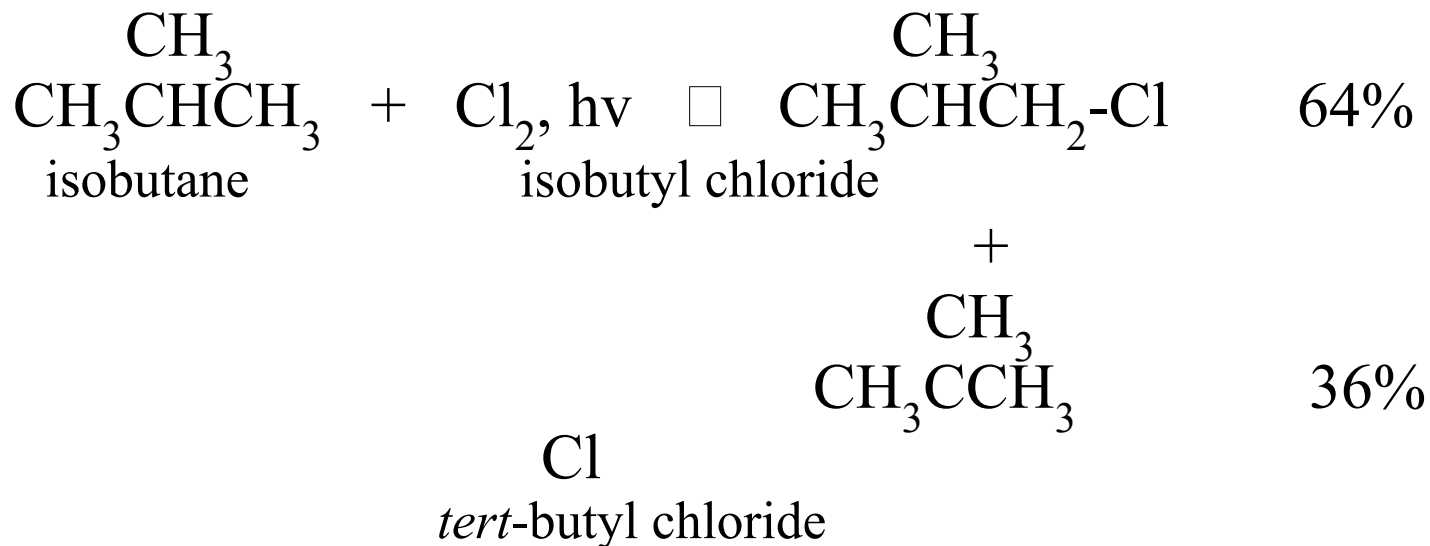
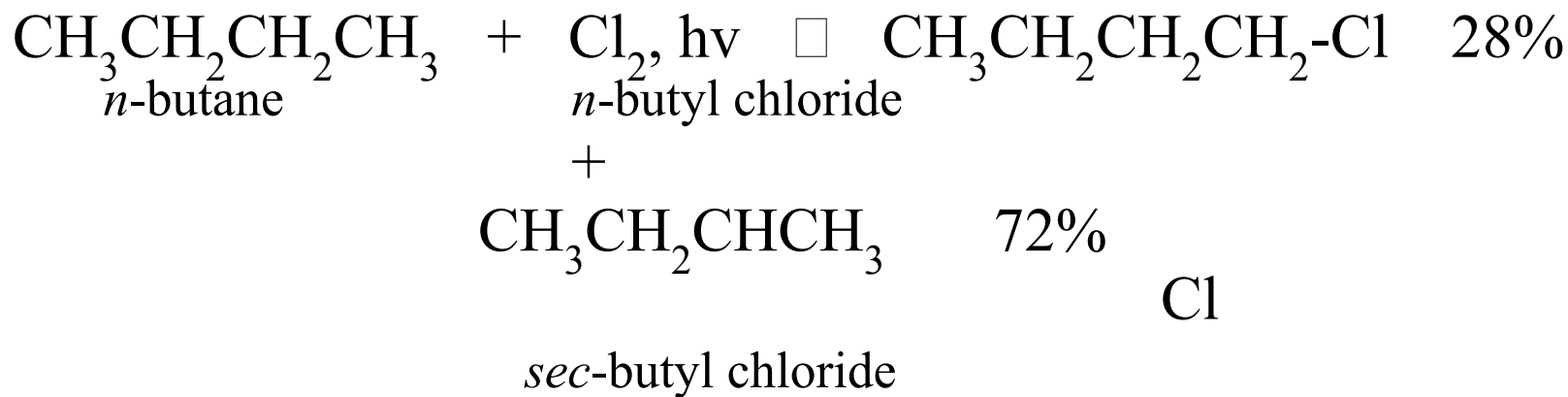
c) yields **mixtures** 😞

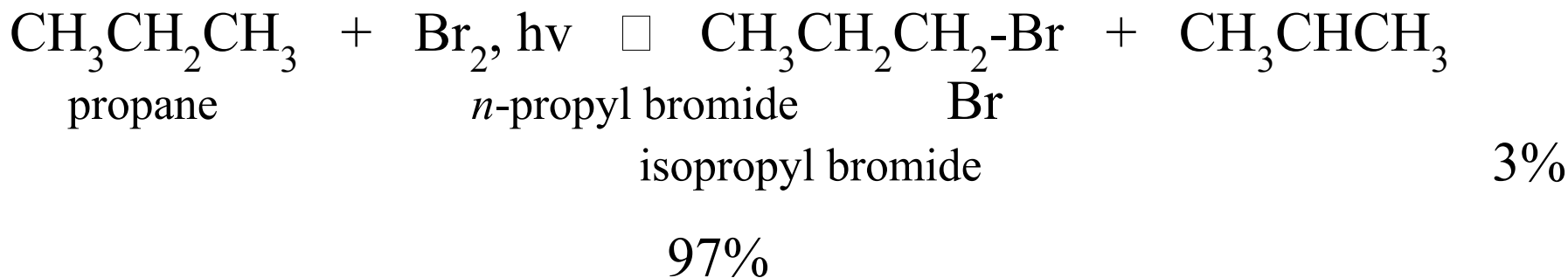
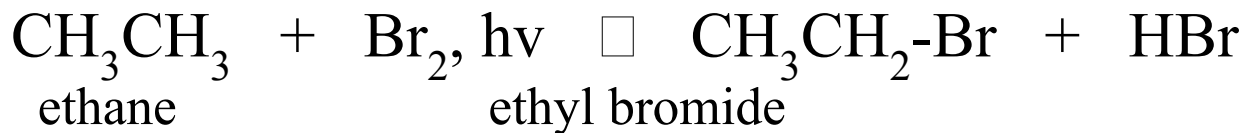
d) H: $3^\circ > 2^\circ > 1^\circ > \text{CH}_4$

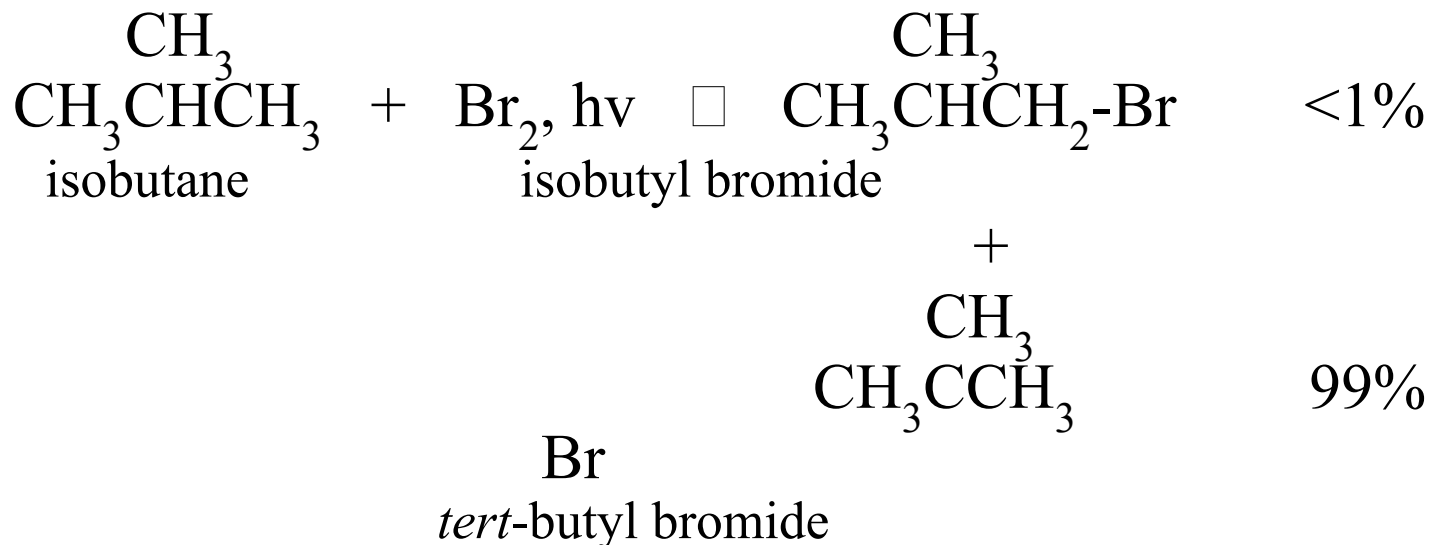
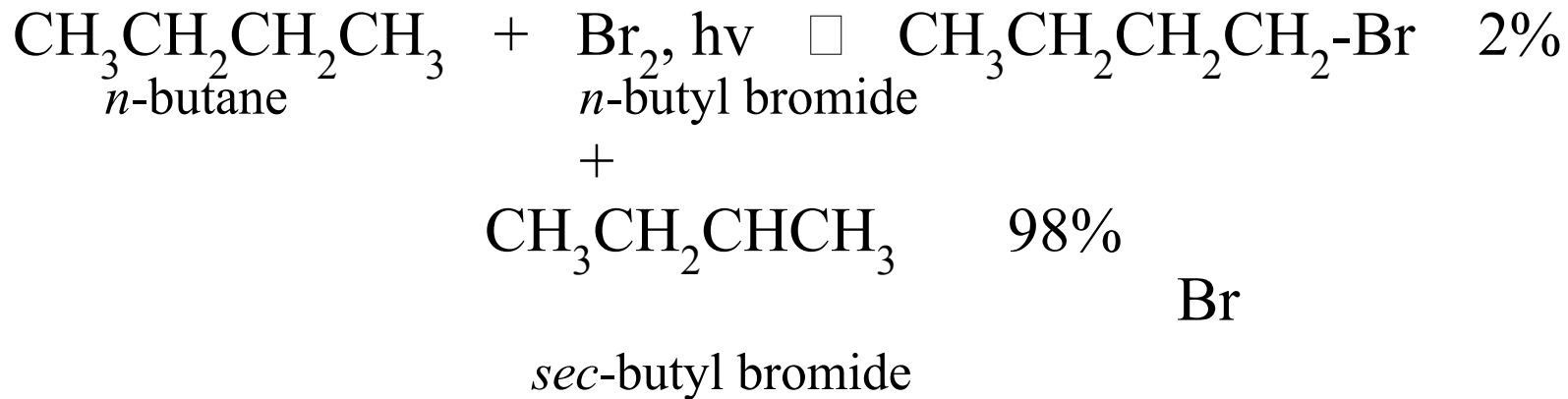
e) bromine is more selective



gives a **mixture** of both the possible alkyl halides! 😞







In the reaction of alkanes with halogens, bromine is less reactive but more selective. Why? How? mechanism:

initiating step:



propagating steps:



2), 3), 2), 3)...

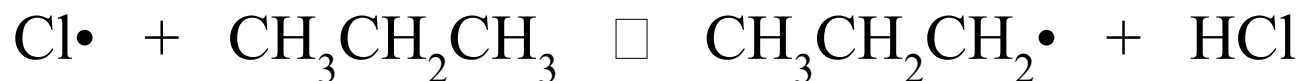
terminating steps:



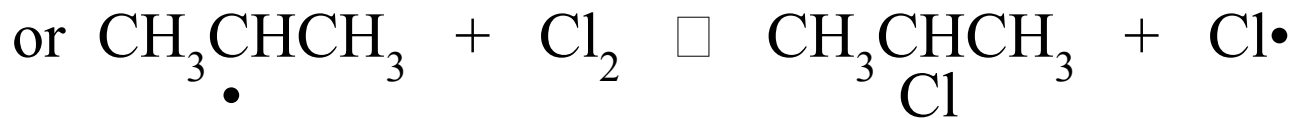
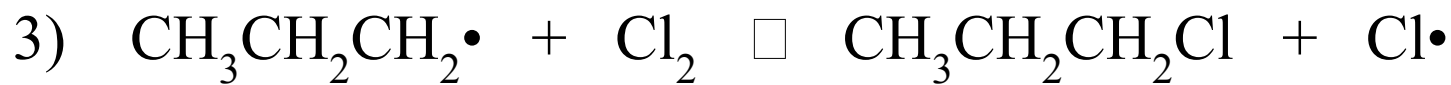
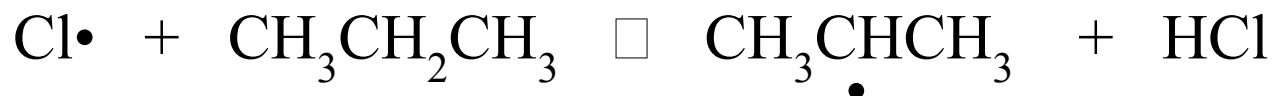
chlorination of propane, mechanism:



2) abstraction of 1° hydrogen:

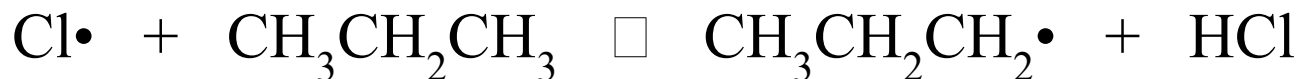


or abstraction of 2° hydrogen:

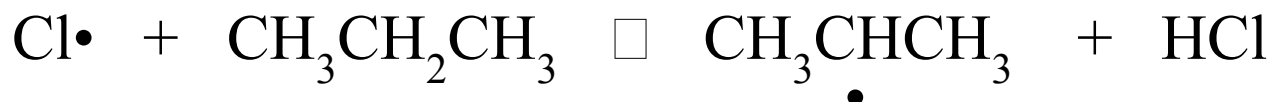


plus terminating steps

2) abstraction of 1° hydrogen:

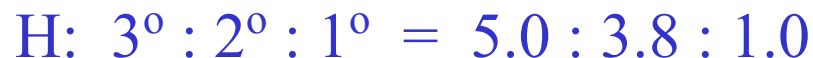


or abstraction of 2° hydrogen:

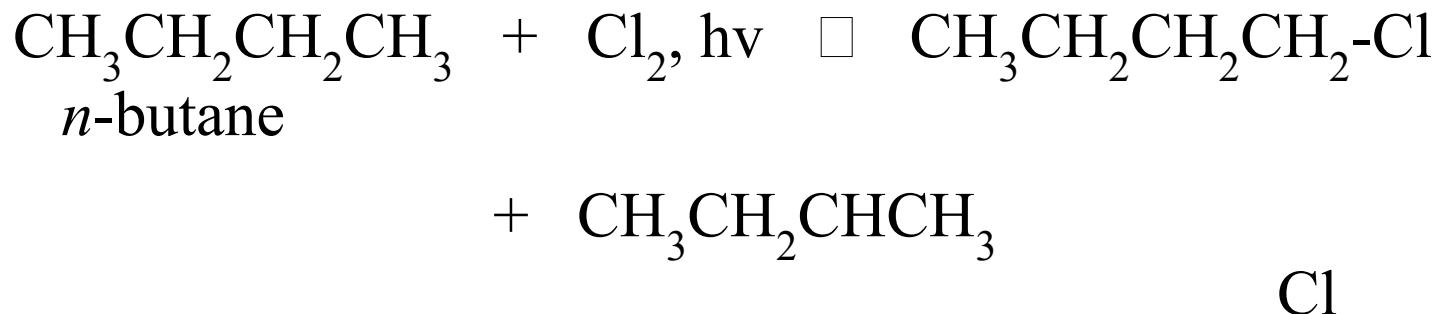


The chloride that is produced depends on which hydrogen is abstracted by the chlorine free radical in step 2. The *n*-propyl free radical gives the *n*-propyl chloride while the isopropyl free radical yields the isopropyl chloride.

The relative reactivity in chlorination:



The number of hydrogens (probability factor) may also be important.

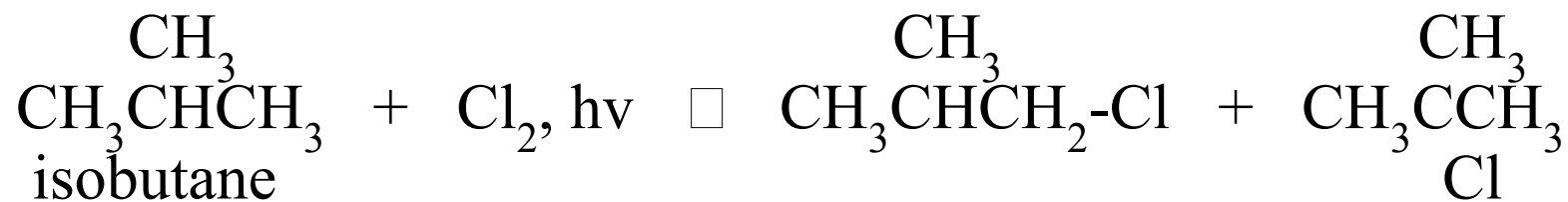


$$\begin{aligned} \text{\textit{n}-butyl chloride} &= (\# \text{ of } 1^\circ \text{ hydrogens}) \times (\text{reactivity of } 1^\circ) \\ &= 6 \times 1.0 = 6.0 \end{aligned}$$

$$\begin{aligned} \text{\textit{sec}-butyl chloride} &= (\# \text{ of } 2^\circ \text{ hydrogens}) \times (\text{reactivity of } 2^\circ) \\ &= 4 \times 3.8 = 15.2 \end{aligned}$$

$$\% \text{\textit{n}-butyl chloride} = 6.0 / (6.0 + 15.2) \times 100\% = 28\%$$

$$\% \text{\textit{sec}-butyl chloride} = 15.2 / (6.0 + 15.2) \times 100\% = 72\%$$



$$\begin{aligned}
 \text{isobutyl chloride} &= (\# \text{ of } 1^\circ \text{ H's}) \times (\text{reactivity of } 1^\circ) \\
 &= 9 \times 1.0 = 9.0
 \end{aligned}$$

$$\begin{aligned}
 \text{tert-butyl chloride} &= (\# \text{ of } 3^\circ \text{ H's}) \times (\text{reactivity of } 3^\circ) \\
 &= 1 \times 5.0 = 5.0
 \end{aligned}$$

$$\% \text{ isobutyl} = (9.0 / (9.0 + 5.0)) \times 100\% = 64\%$$

In this case the probability factor outweighs the difference in relative reactivity of 1° and 3° hydrogens.

Relative reactivity in bromination:

$$3^\circ : 2^\circ : 1^\circ = 1600 : 82 : 1$$

In bromination the relative reactivity differences are much greater than any probability differences.

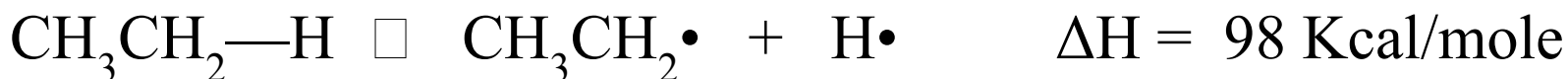
isobutane + Br₂, hv \square isobutyl bromide + *tert*-butyl bromide

isobutyl bromide = 9 H x 1 = 9

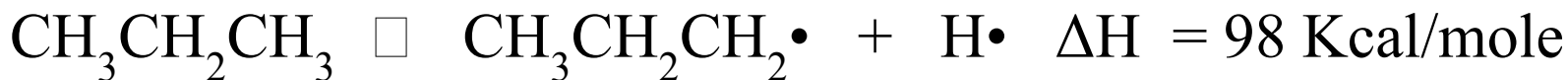
tert-butyl bromide = 1 H x 1600 = 1600

% *tert*-butyl bromide = (1600/1601) x 100% = >99%

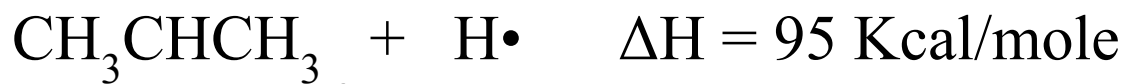
Why is relative reactivity of H: $3^\circ > 2^\circ > 1^\circ$?



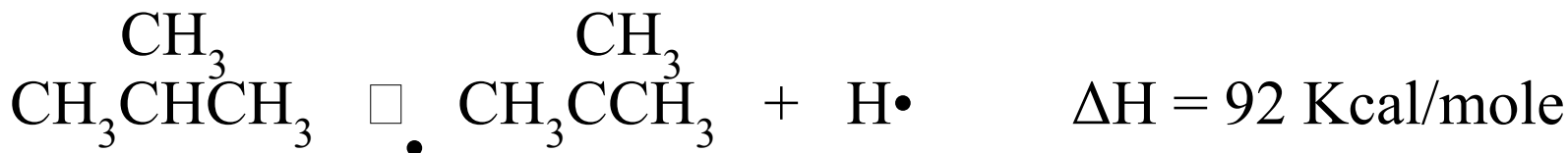
1° free radical



1° free radical



2° free radical



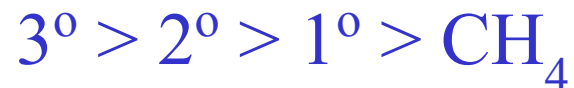
3° free radical

Relative reactivity in halogenation:

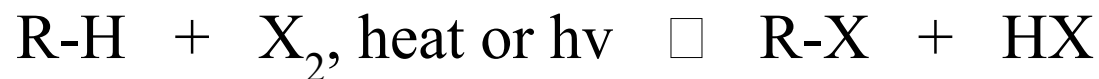
Stability of free radicals:

Ease of formation of free radicals:

Ease of abstraction of H's:



1. Halogenation



a) heat or light required for reaction.

b) X_2 : $\text{Cl}_2 > \text{Br}_2 \neq \text{I}_2$

c) yields **mixtures** 😞

d) H: $3^\circ > 2^\circ > 1^\circ > \text{CH}_4$

e) bromine is more selective

Alkane, reactions:

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2. Combustion (oxidation)
3. Pyrolysis (cracking)