Alkanes

ALKANES

(a “family” of hydrocarbons)

C_nH_{2n+2} CH_4

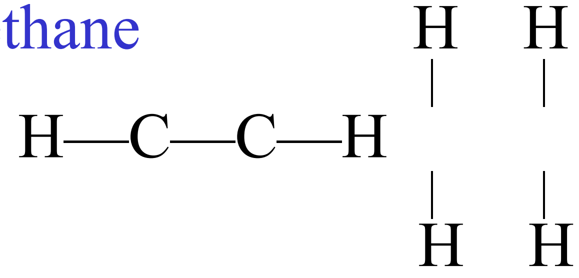
C_2H_6

C_3H_8

C_4H_{10}

etc.

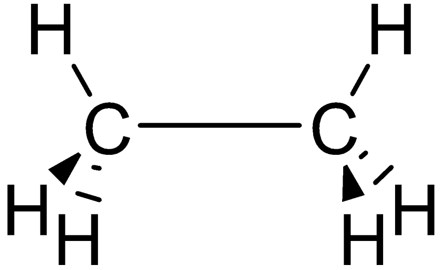
C_2H_6 ethane



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

sp^3, bond angles = 109.5^o

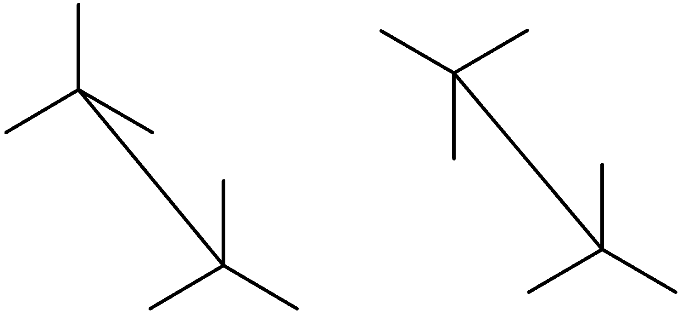
σ-bonds (sigma)

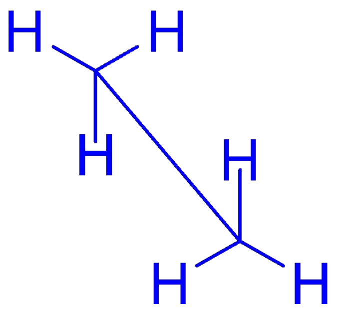


rotation about C--C (conformations)

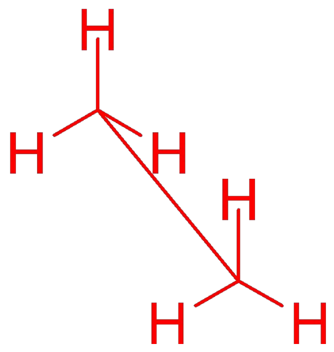
representation:

“andiron” or “sawhorse”





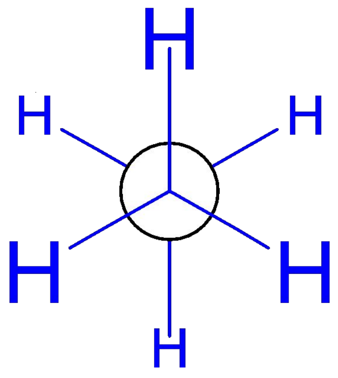
“staggered”

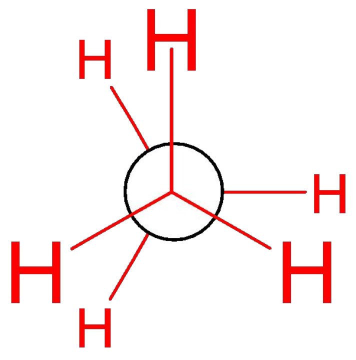


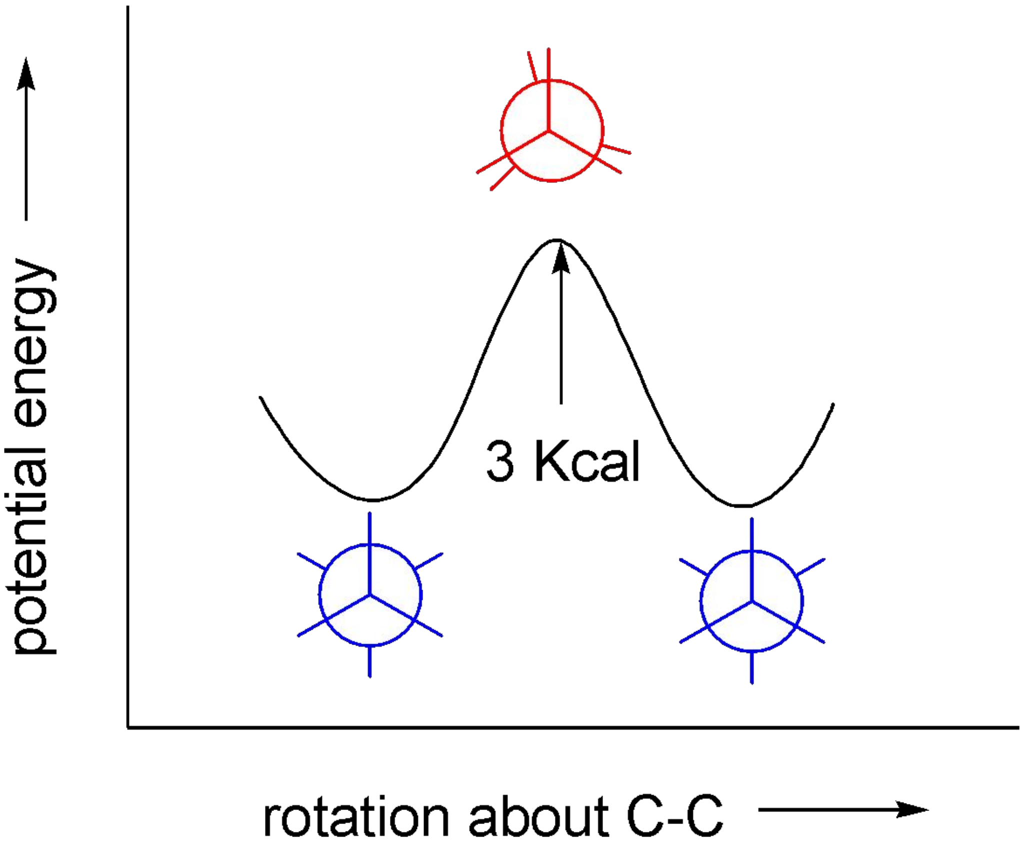
“eclipsed”

torsional strain: deviation from staggered.

Newman projections:

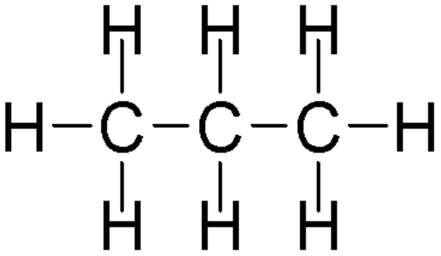






The barrier to rotation about the carbon-carbon bond in ethane is 3 Kcal/mole. The rotation is ~ “free.”

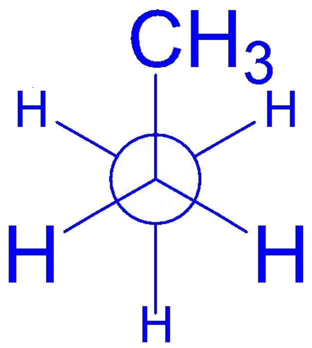
C_3H_8 propane



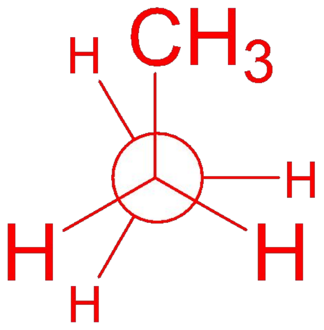
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

projection formula

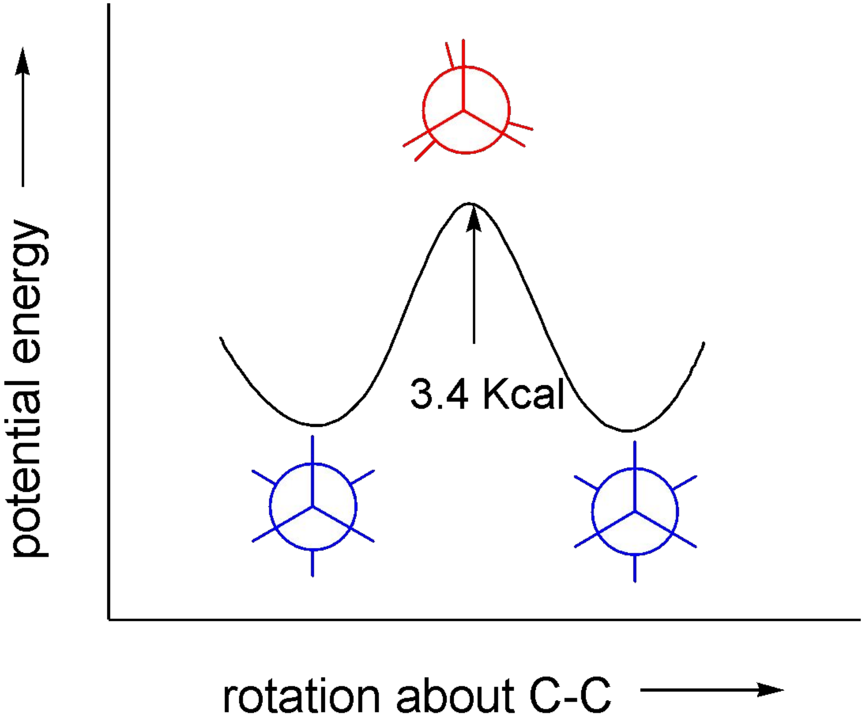
$CH_3CH_2CH_3$ partially condensed formula



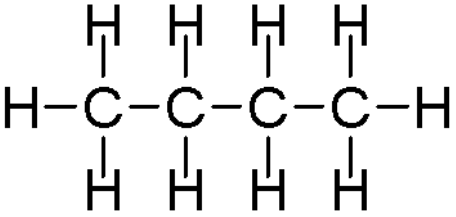
staggered

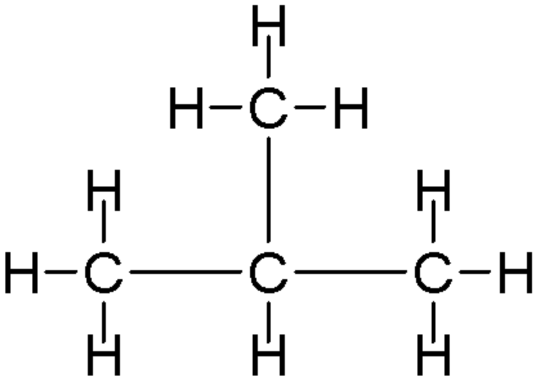


eclipsed



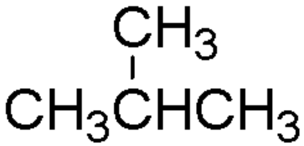
C_4H_{10} butane(s)





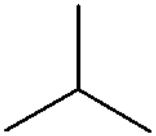
projection

$CH_3CH_2CH_2CH_3$



$$\begin{array}{c} CH_3 \\ | \\ CH_3CHCH_3 \end{array}$$

partially condensed

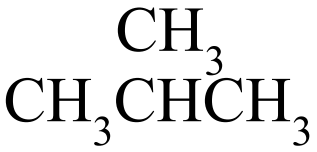


stick formulas

Two isomers of butane C_4H_{10}:

$CH_3CH_2CH_2CH_3$ *n*-butane

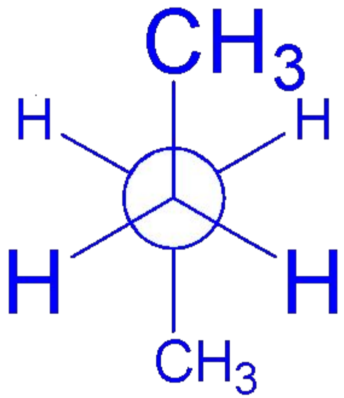
bp 0 °C
mp –138 °C
d 0.622 g/cc



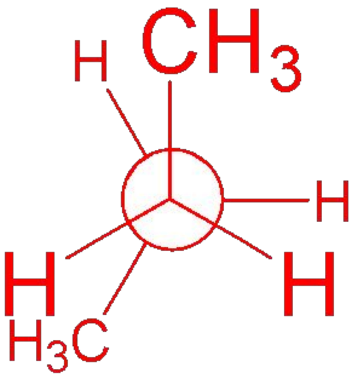
$\overset{CH_3}{CH_3CHCH_3}$ isobutane

bp -12 °C
mp -159 °C
d 0.604 g/cc

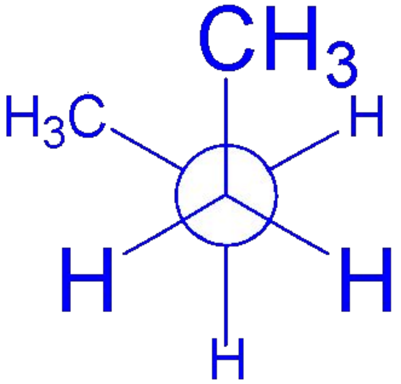
Conformations about C2-C3 in *n*-butane:



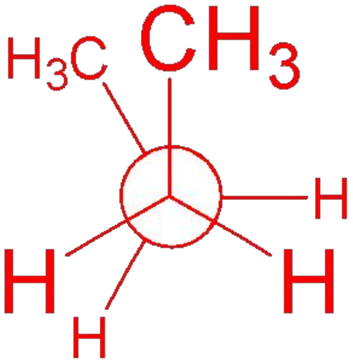
anti



CH_3/H eclipsed

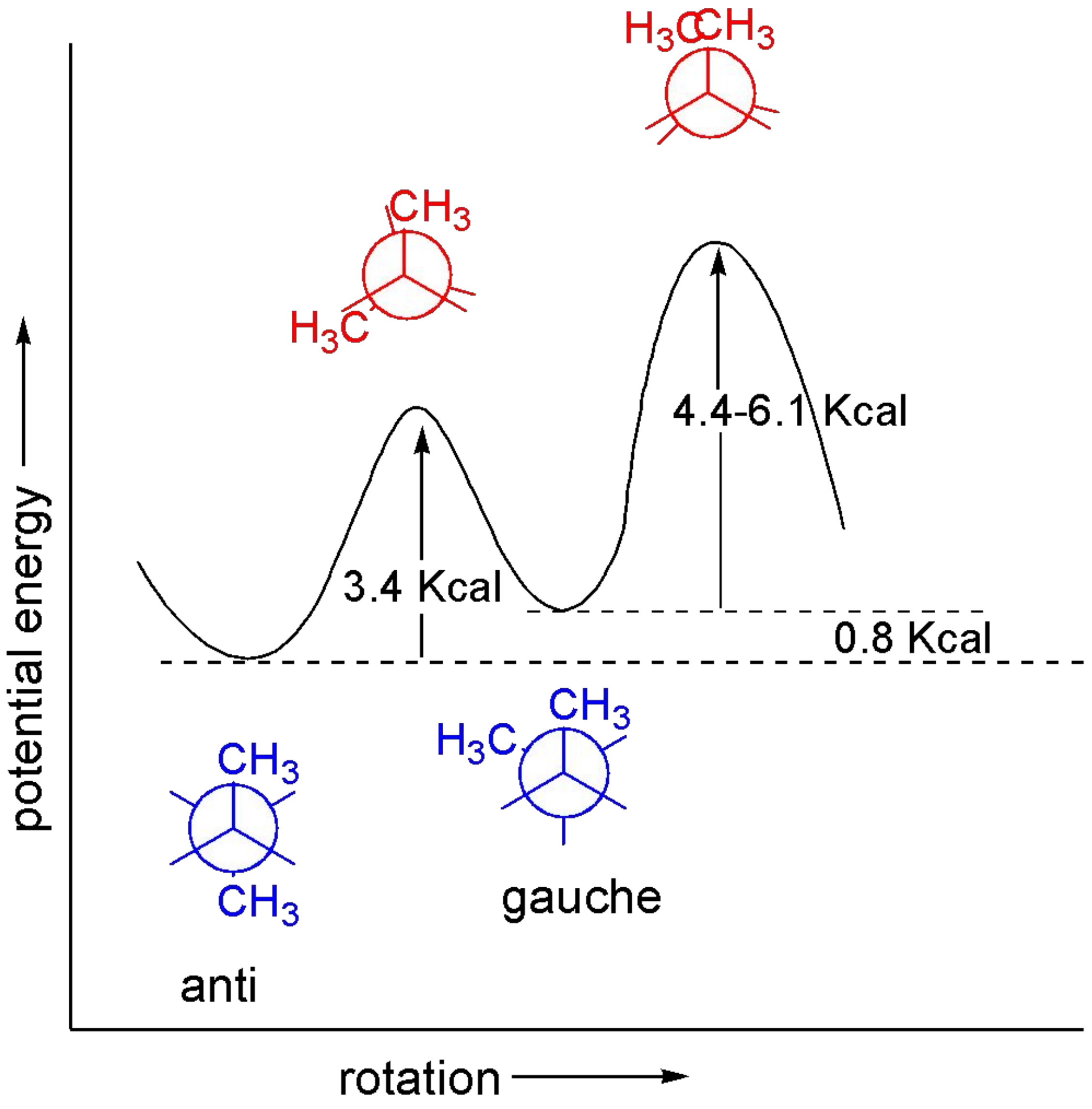


gauche



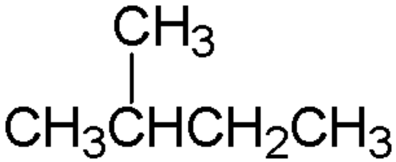
CH_3/CH_3 eclipsed

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



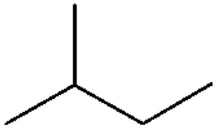
C_5H_{12} pentane(s)

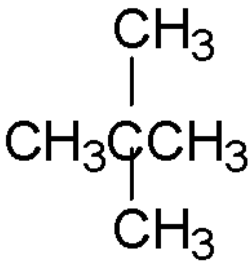
$CH_3CH_2CH_2CH_2CH_3$ *n-pentane*



$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$$

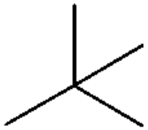
isopentane





$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$$

neopentane



these are common, or trivial, names where a prefix is used to idicate 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
$C_{10}H_{22}$	decanes	75
…….		
$C_{20}H_{42}$	eicosanes	366,319

each new common name requires a new prefix…

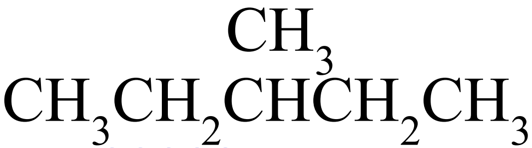
hexanes C_6H_{14} common names

$CH_3CH_2CH_2CH_2CH_2CH_3$

n-hexane

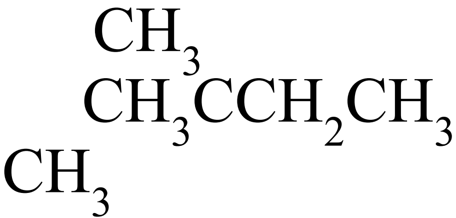
$CH_3\overset{CH_3}{C}HCH_2CH_2CH_3$

isohexane



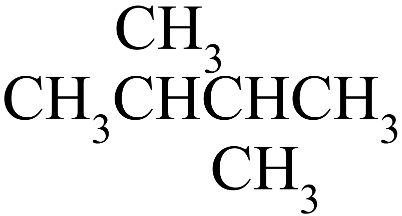
$CH_3CH_2\overset{CH_3}{C}HCH_2CH_3$

?????



$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$

neohexane



$CH_3\overset{CH_3}{C}H\underset{CH_3}{C}HCH_3$

????

IUPAC nomenclature (Geneva, 1920)

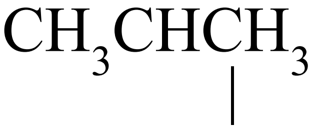
names of radicals (alkyl groups):

CH_3- “methyl” CH_3Cl methyl chloride

CH_3OH methyl alcohol, etc.

CH_3CH_2- “ethyl”

$CH_3CH_2CH_2$- “*n*-propyl”



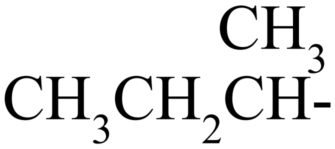
CH_3CHCH_3

“isopropyl”

$\mathrm{CH_3CH_2CH_2CH_2}$- “*n*-butyl”

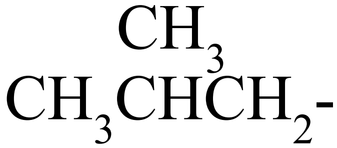
$\mathrm{CH_3CH_2\underset{|}{C}HCH_3}$

or



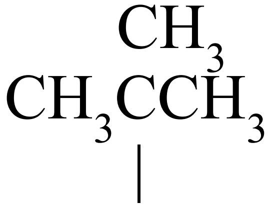
$\mathrm{CH_3CH_2\overset{CH_3}{C}H}$-

“*sec*-butyl”



$\mathrm{CH_3\overset{CH_3}{C}HCH_2}$-

“isobutyl”



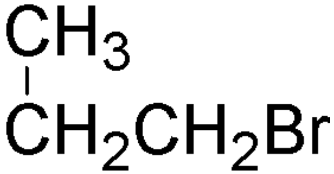
$\mathrm{CH_3\underset{|}{\overset{CH_3}{C}}CH_3}$

“*tert*-butyl”

n-propyl bromide

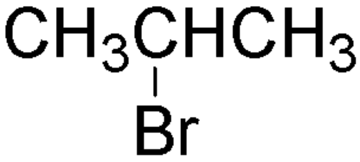
$CH_3CH_2CH_2Br$

$BrCH_2CH_2CH_3$

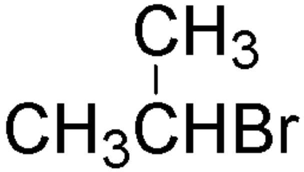


$$\begin{array}{l} CH_3 \\ | \\ CH_2CH_2Br \end{array}$$

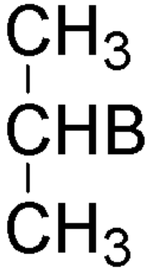
isopropyl bromide



$$\begin{array}{l} CH_3CHCH_3 \\ \quad\;\;\, | \\ \quad\;\;\, Br \end{array}$$



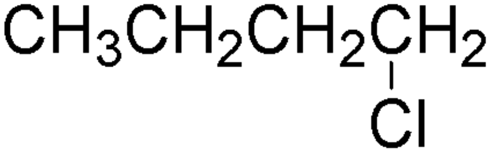
$$\begin{array}{l} \quad\;\;\, CH_3 \\ \quad\;\;\, | \\ CH_3CHBr \end{array}$$



$$\begin{array}{l} CH_3 \\ | \\ CHBr \\ | \\ CH_3 \end{array}$$

n-butyl chloride

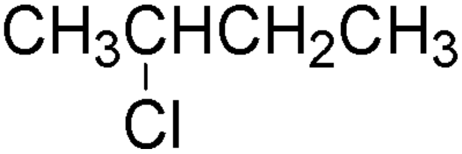
$CH_3CH_2CH_2CH_2Cl$



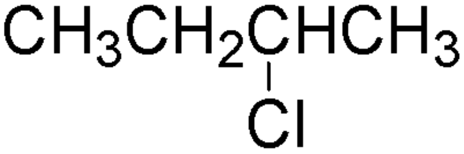
$CH_3CH_2CH_2\underset{\underset{Cl}{|}}{C}H_2$

$ClCH_2CH_2CH_2CH_3$

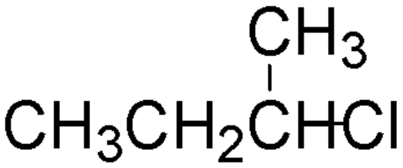
sec-butyl chloride



$CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_3$

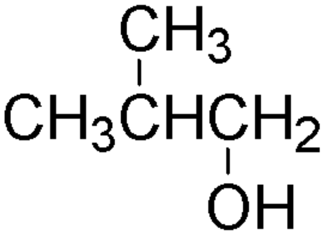


$CH_3CH_2\underset{\underset{Cl}{|}}{C}HCH_3$

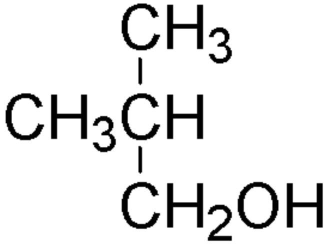


$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCl$

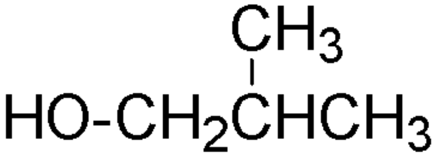
isobutyl alcohol



$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{OH}{|}}{C}H_2}$$

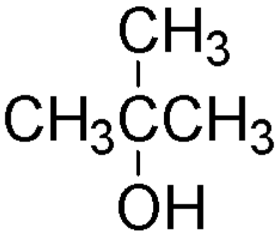


$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2OH}{|}}{C}}H}$$

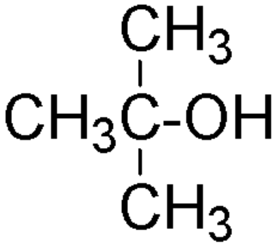


$$\mathrm{HO\text{-}CH_2\overset{\overset{CH_3}{|}}{C}HCH_3}$$

tert-butyl alcohol



$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}CH_3}$$



$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}OH}$$

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

$CH_3CH_2CH_2CH_2CH_2CH_3$

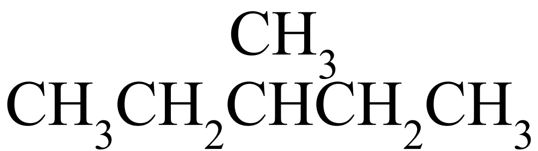
(*n*-hexane)

n-hexane

$CH_3\overset{CH_3}{C}HCH_2CH_2CH_3$

(isohexane)

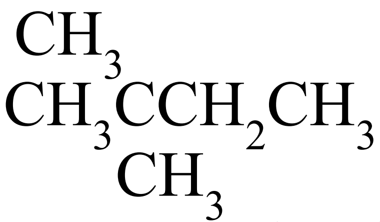
2-methylpentane



$CH_3CH_2\overset{CH_3}{C}HCH_2CH_3$

(no common name)

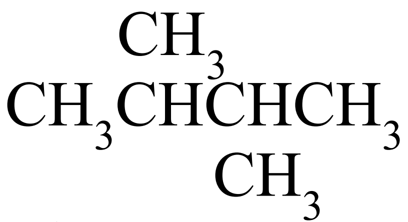
3-methylpentane



$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$

(neohexane)

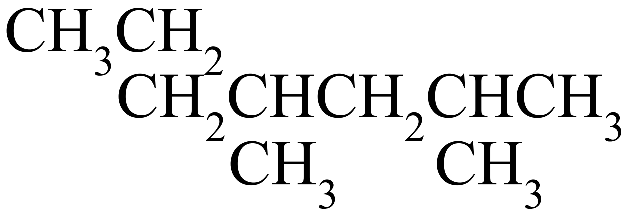
2,2-dimethylbutane



$CH_3\underset{CH_3}{C}H\overset{CH_3}{C}HCH_3$

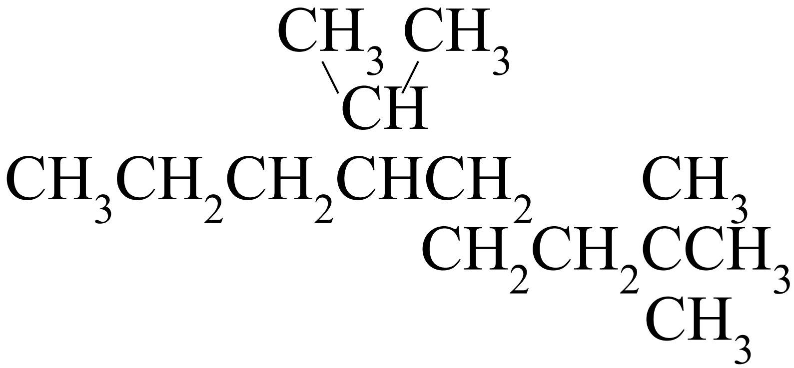
(no common name)

2,3-dimethylbutane



$$\begin{array}{l} CH_3CH_2 \\ \quad\quad CH_2CHCH_2CHCH_3 \\ \quad\quad\quad\quad CH_3 \quad\quad CH_3 \end{array}$$

2,4-dimethylheptane



$$\begin{array}{l} \quad\quad\quad\quad\quad CH_3 \;\; CH_3 \\ \quad\quad\quad\quad\quad\quad \backslash \;\; / \\ \quad\quad\quad\quad\quad\quad\; CH \\ CH_3CH_2CH_2CHCH_2 \quad\quad CH_3 \\ \quad\quad\quad\quad\quad\quad\quad\; CH_2CH_2CCH_3 \\ \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\;\; CH_3 \end{array}$$

6-isopropyl-2,2-dimethylnonane

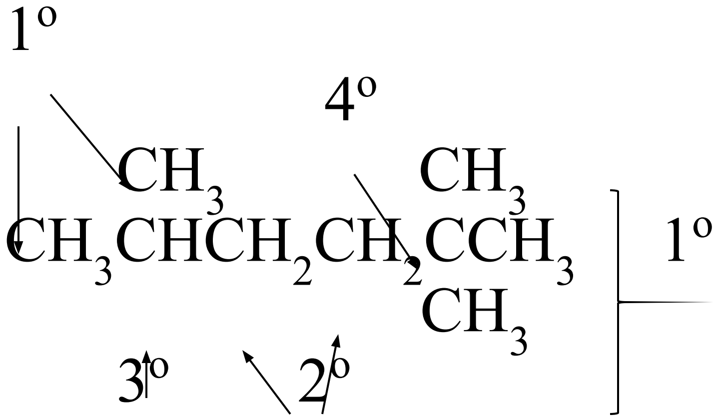
“**classes** of carbons”

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

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

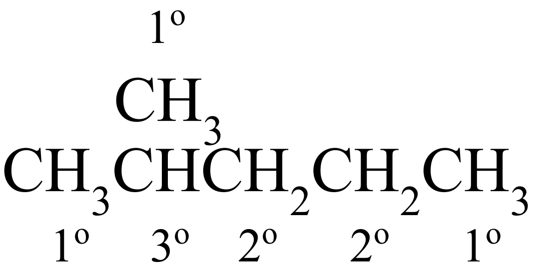
tertiary carbon (3°) – a carbon bonded to three carbons

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



$$CH_3\overset{CH_3}{CH}CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_3$$

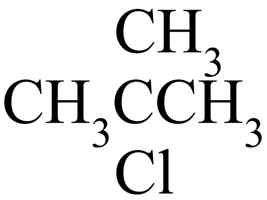
classification of hydrogens, halides – hydrogens or halides are classified by the carbon to which they are attached.



$$\underset{1^\circ}{CH_3}\underset{3^\circ}{\overset{\overset{1^\circ}{CH_3}}{CH}}\underset{2^\circ}{CH_2}\underset{2^\circ}{CH_2}\underset{1^\circ}{CH_3}$$

$$CH_3CH_2\underset{Br}{CH}CH_3$$

sec-butyl bromide 2° bromide



$$CH_3\overset{CH_3}{\underset{Cl}{C}}CH_3$$

tert-butyl chloride 3° chloride

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

alkane	mp ºC	bp ºC
methane	-183	-162
ethane	-172	-89
propane	-187	-42
n-butane	-138	0
n-pentane	-130	36
n-hexane	-95	69
…		
n-heptadecane	22	292
n-octadecane	28	308

branching lowers mp/bp

n-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-volaltile liquids	
asphalt	non-volatile solids	
coke	solid carbon	

syntheses

Industrial	Laboratory
large amounts (tons)	small amounts (grams)
lowest cost	non-profit
mixtures often okay	pure substances
dedicated apparatus	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)

i) $R{-}X$ + Mg □ $RMgX$ (Grignard reagent)

ii) $RMgX$ + H_2O □ RH + $Mg(OH)X$

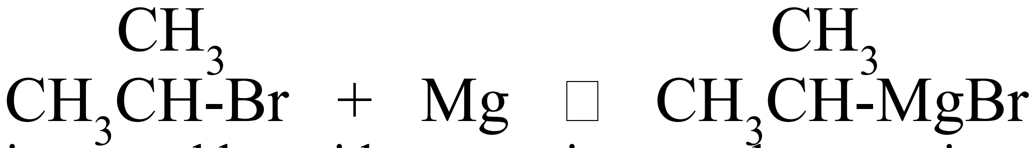
SB SA WA WB

$CH_3CH_2CH_2$-Br + Mg □ $CH_3CH_2CH_2$-$MgBr$

n-propyl bromide *n*-propyl magnesium bromide

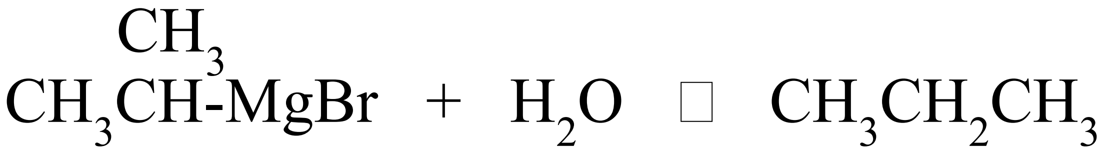
$CH_3CH_2CH_2$-$MgBr$ + H_2O □ $CH_3CH_2CH_3$ + $Mg(OH)Br$

propane



$$\mathrm{CH_3\overset{CH_3}{CH}\text{-}Br} \quad + \quad \mathrm{Mg} \quad \square \quad \mathrm{CH_3\overset{CH_3}{CH}\text{-}MgBr}$$

isopropyl bromide　　　　isopropyl magnesium bromide

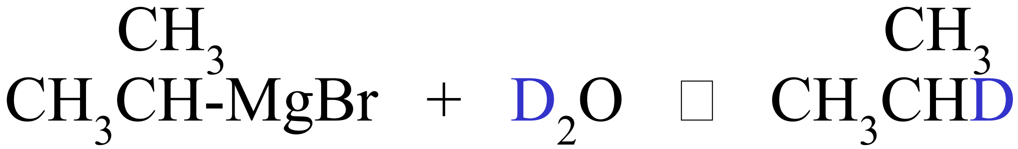


$$\mathrm{CH_3\overset{CH_3}{CH}\text{-}MgBr} \quad + \quad \mathrm{H_2O} \quad \square \quad \mathrm{CH_3CH_2CH_3}$$

propane

$$\mathrm{CH_3CH_2CH_2\text{-}MgBr} \quad + \quad \mathrm{D_2O} \quad \square \quad \mathrm{CH_3CH_2CH_2D}$$

heavy water



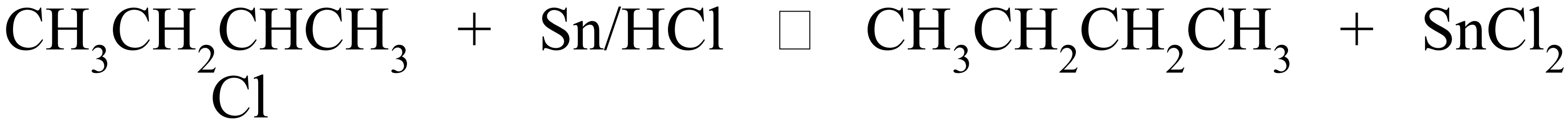
$$\mathrm{CH_3\overset{CH_3}{CH}\text{-}MgBr} \quad + \quad \mathrm{D_2O} \quad \square \quad \mathrm{CH_3\overset{CH_3}{CH}D}$$

b) with an active metal and an acid

R—X + metal/acid □ RH

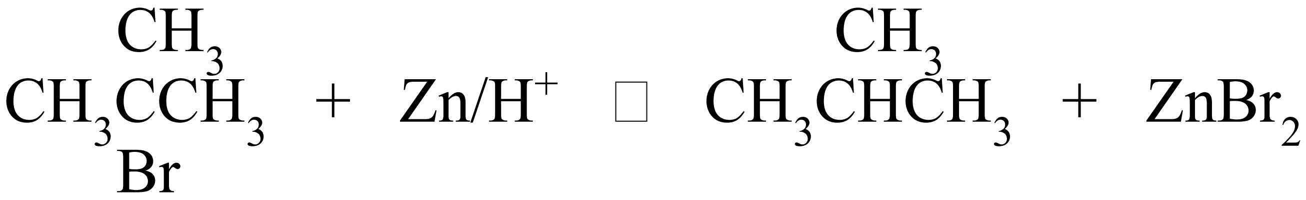
active metals = Sn, Zn, Fe, etc.

acid = HCl, etc. (H^+)



$$CH_3CH_2\underset{Cl}{CH}CH_3 + Sn/HCl \; \square \; CH_3CH_2CH_2CH_3 + SnCl_2$$

sec-butyl chloride n-butane



$$CH_3\underset{Br}{\overset{CH_3}{C}}CH_3 + Zn/H^+ \; \square \; CH_3\overset{CH_3}{CH}CH_3 + ZnBr_2$$

tert-butyl bromide isobutane

3. Corey-House synthesis

$$\text{R-X} \;+\; \text{Li} \;\square\; \text{R-Li} \;+\; \text{CuI} \;\square\; \text{R}_2\text{CuLi}$$

$$\text{R}_2\text{CuLi} \;+\; \text{R}'\text{-X} \;\square\; \text{R—R}' \;\; \text{(alkane)}$$

(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.

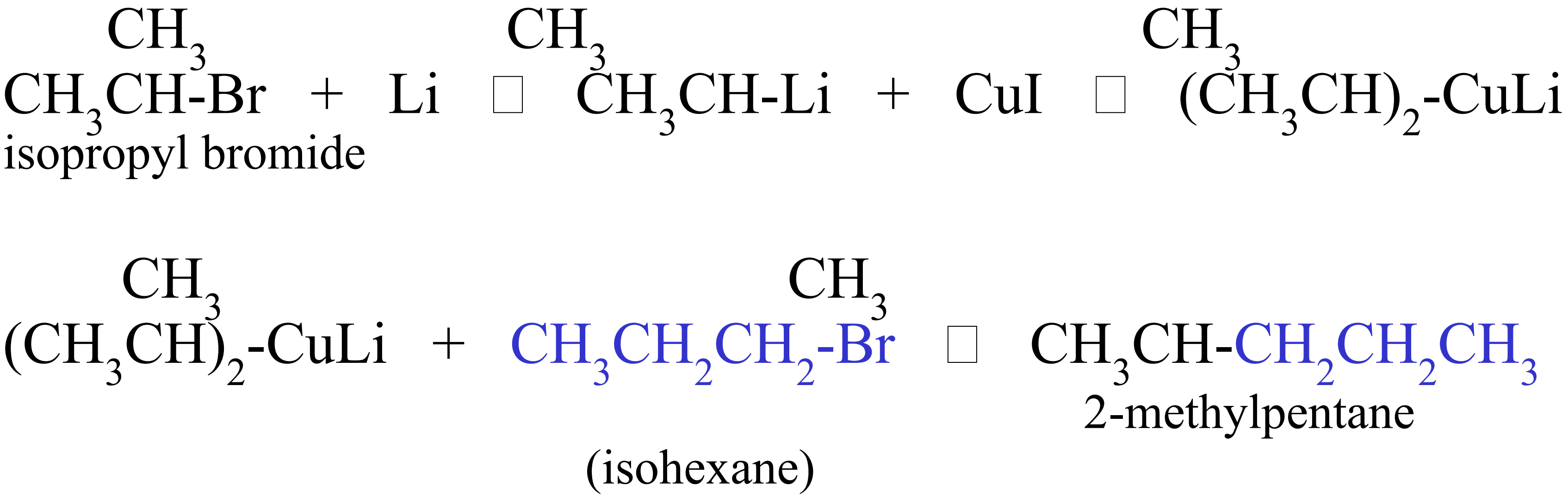
note: the previous equations are not balanced:

$$\mathrm{R\text{-}X} \;+\; 2\,\mathrm{Li} \;\;\square\;\; \mathrm{R\text{-}Li} \;+\; \mathrm{LiX}$$

$$2\,\mathrm{R\text{-}Li} \;+\; \mathrm{CuI} \;\;\square\;\; \mathrm{R_2CuLi} \;+\; \mathrm{LiX}$$

$$\mathrm{R_2CuLi} \;=\; \mathrm{R\text{-}Cu^-,\ Li^{\overset{R}{+}}}$$

$$\mathrm{R_2CuLi} \;+\; \mathrm{R'X} \;\;\square\;\; \mathrm{R\text{-}R'} \;+\; \mathrm{RCu} \;+\; \mathrm{LiX}$$



$$\overset{\mathrm{CH_3}}{\mathrm{CH_3CH}}\text{-}\mathrm{Br} \;+\; \mathrm{Li} \;\square\; \overset{\mathrm{CH_3}}{\mathrm{CH_3CH}}\text{-}\mathrm{Li} \;+\; \mathrm{CuI} \;\square\; (\overset{\mathrm{CH_3}}{\mathrm{CH_3CH}})_2\text{-}\mathrm{CuLi}$$

isopropyl bromide

$$(\overset{\mathrm{CH_3}}{\mathrm{CH_3CH}})_2\text{-}\mathrm{CuLi} \;+\; \mathrm{CH_3CH_2}\overset{\mathrm{CH_3}}{\mathrm{CH_2\text{-}Br}} \;\square\; \mathrm{CH_3CH\text{-}CH_2CH_2CH_3}$$

2-methylpentane

(isohexane)

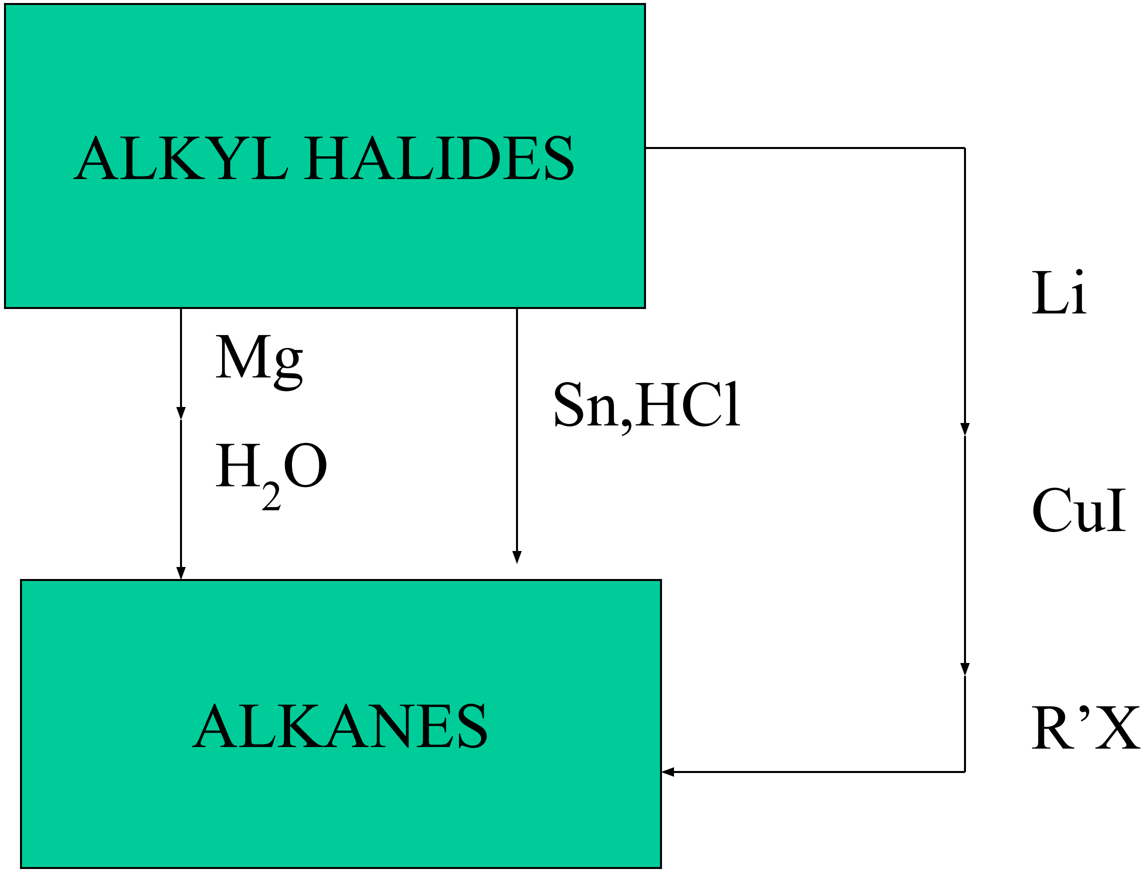
Note: the R´X should be a 1° or methyl halide for the best yields of the final product.

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)



ALKYL HALIDES

Mg

H_2O

Sn,HCl

Li

CuI

R’X

ALKANES

Reactions of alkanes:

alkane + H_2SO_4 □ no reaction (NR)

alkane + NaOH □ NR

alkane + Na □ NR

alkane + $KMnO_4$ □ NR

alkane + H_2,Ni □ NR

alkane + Br_2 □ NR

alkane + H_2O □ NR

(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

C_nH_{2n+2} + (xs) O_2, flame → n CO_2 + (n+1) H_2O + **heat**

gasoline, diesel, heating oil…

3. Pyrolyis (cracking)

alkane, 400-600°C → smaller alkanes + alkenes + H_2

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

R-H + X_2, heat or hv □ R-X + HX

a) heat or light required for reaction.

b) X_2: $Cl_2 > Br_2 \neq I_2$

c) yields **mixtures** ☹️

d) H: $3^{o} > 2^{o} > 1^{o} > CH_4$

e) bromine is more selective

CH_3CH_3 + Cl_2, hv □ CH_3CH_2-Cl + HCl

ethane ethyl chloride

$CH_3CH_2CH_3$ + Cl_2, hv □ $CH_3CH_2CH_2$-Cl + $\underset{Cl}{CH_3CHCH_3}$

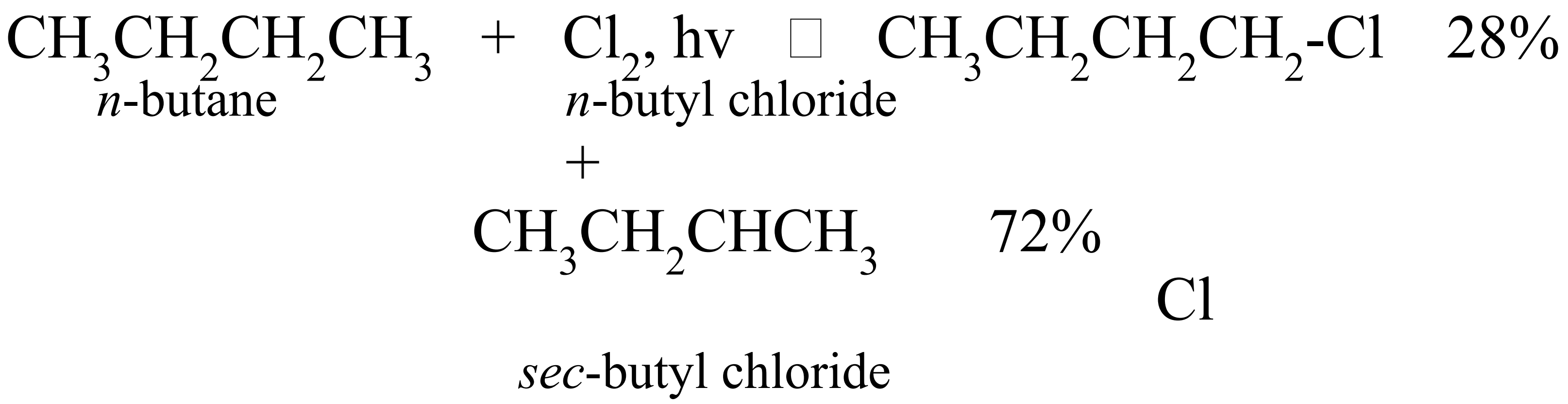
propane *n*-propyl chloride

isopropyl chloride

45%

55%

gives a mixture of both the possible
alkyl halides! ☹



$CH_3CH_2CH_2CH_3$ + Cl_2, hv □ $CH_3CH_2CH_2CH_2$-Cl 28%

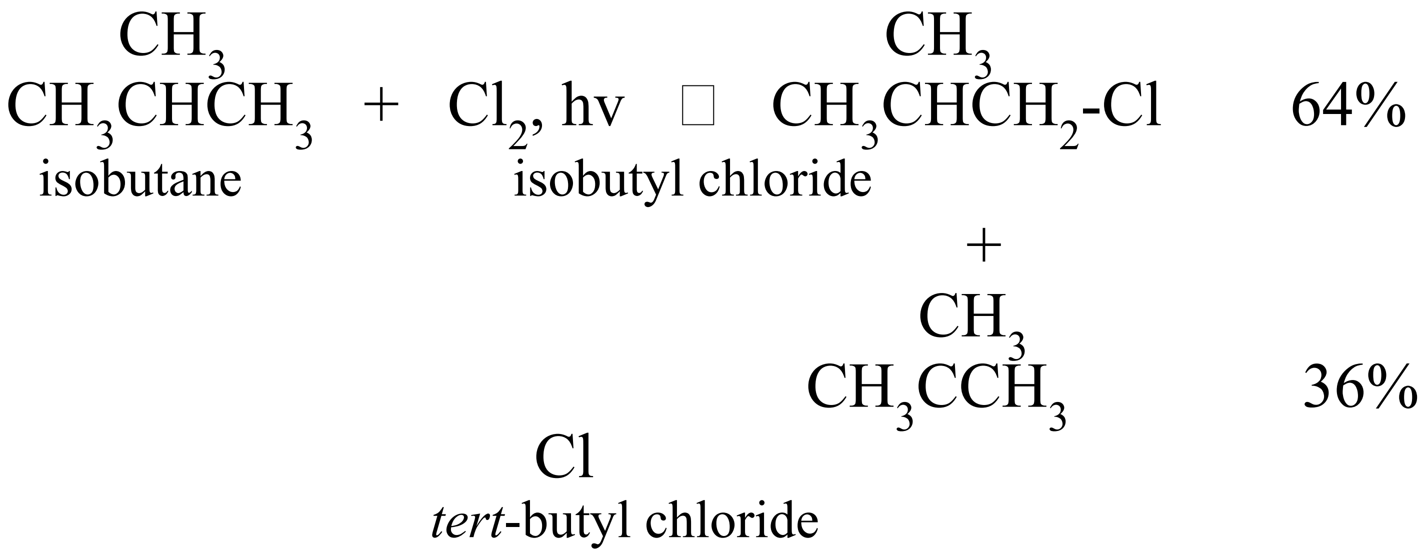
n-butane *n*-butyl chloride

+

$CH_3CH_2CHCH_3$ 72%

Cl

sec-butyl chloride



CH_3 CH_3

CH_3CHCH_3 + Cl_2, hv □ CH_3CHCH_2-Cl 64%

isobutane isobutyl chloride

+

CH_3

CH_3CCH_3 36%

Cl

tert-butyl chloride

CH_3CH_3 + Br_2, hv □ CH_3CH_2-Br + HBr

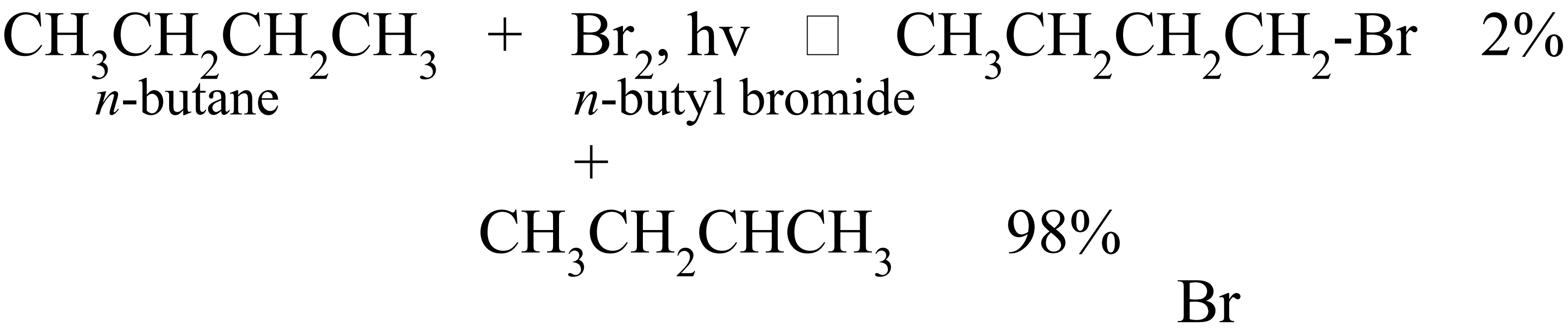
ethane ethyl bromide

$CH_3CH_2CH_3$ + Br_2, hv □ $CH_3CH_2CH_2$-Br + CH_3CHCH_3

propane *n*-propyl bromide Br

isopropyl bromide 3%

97%



$$CH_3CH_2CH_2CH_3 \quad + \quad Br_2,\ hv \ \rightarrow \ CH_3CH_2CH_2CH_2\text{-}Br \quad 2\%$$

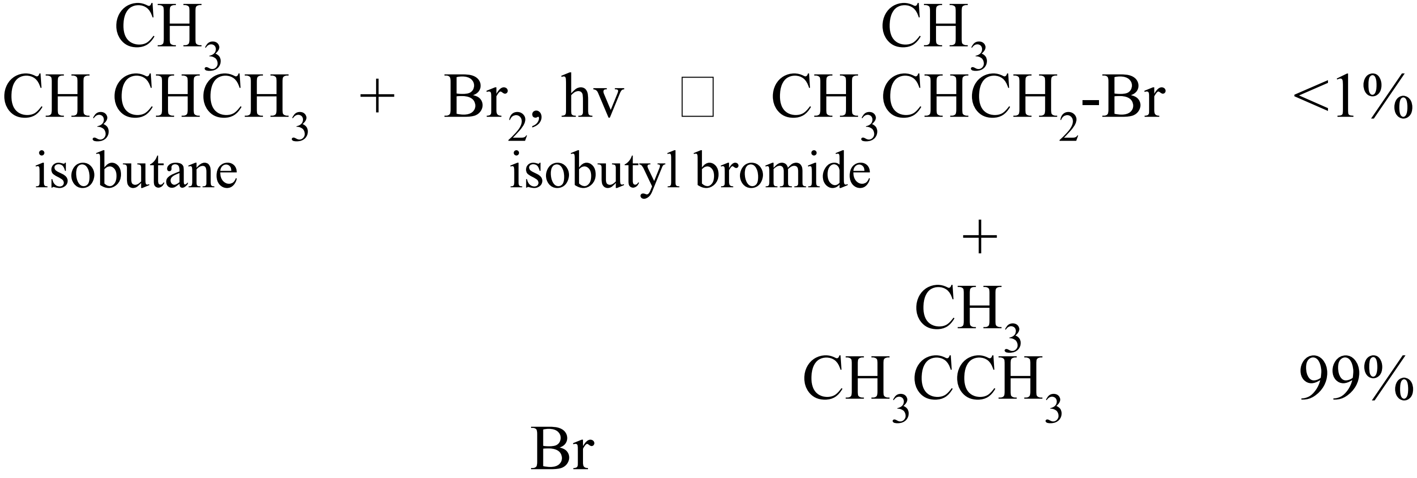
n-butane

n-butyl bromide

+

$$CH_3CH_2\underset{Br}{CH}CH_3 \quad 98\%$$

sec-butyl bromide



$$CH_3\overset{CH_3}{CH}CH_3 \quad + \quad Br_2,\ hv \ \rightarrow \ CH_3\overset{CH_3}{CH}CH_2\text{-}Br \quad <1\%$$

isobutane

isobutyl bromide

+

$$CH_3\underset{Br}{\overset{CH_3}{C}}CH_3 \quad 99\%$$

tert-butyl bromide

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

initiating step:

1) X—X □ 2 X•

propagating steps:

2) X• + R—H □ H—X + R•

3) R• + X—X □ R—X + X•

2), 3), 2), 3)…

terminating steps:

4) 2 X• □ X—X

5) R• + X• □ R—X

6) 2 R• □ R—R

chlorination of propane, mechanism:

1) Cl—Cl □ 2 Cl•

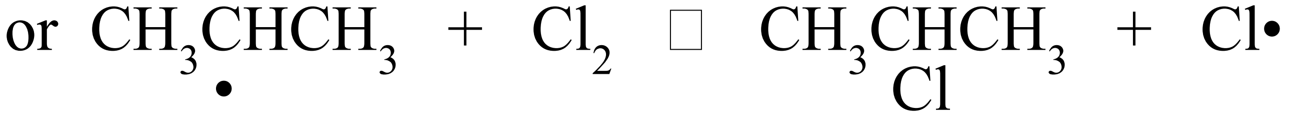
2) abstraction of 1° hydrogen:

$Cl\bullet + CH_3CH_2CH_3$ □ $CH_3CH_2CH_2\bullet + HCl$

or abstraction of 2° hydrogen:

$Cl\bullet + CH_3CH_2CH_3$ □ $CH_3\underset{\bullet}{C}HCH_3 + HCl$

3) $CH_3CH_2CH_2\bullet + Cl_2$ □ $CH_3CH_2CH_2Cl + Cl\bullet$



or $CH_3\underset{\bullet}{C}HCH_3 + Cl_2$ □ $CH_3\underset{Cl}{C}HCH_3 + Cl\bullet$

plus terminating steps

2) abstraction of 1° hydrogen:

$$\mathrm{Cl\bullet} \quad + \quad \mathrm{CH_3CH_2CH_3} \quad \square \quad \mathrm{CH_3CH_2CH_2\bullet} \quad + \quad \mathrm{HCl}$$

or abstraction of 2° hydrogen:

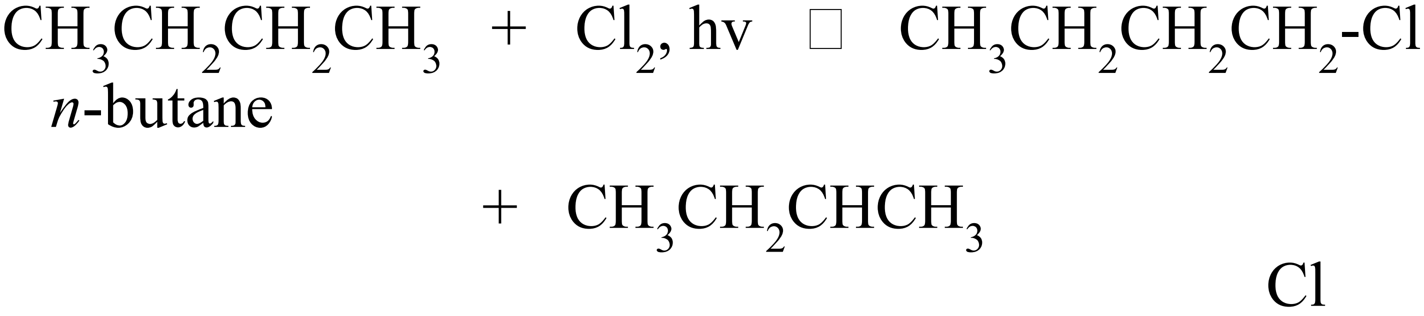
$$\mathrm{Cl\bullet} \quad + \quad \mathrm{CH_3CH_2CH_3} \quad \square \quad \mathrm{CH_3\underset{\bullet}{C}HCH_3} \quad + \quad \mathrm{HCl}$$

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:

H: 3° : 2° : 1° = 5.0 : 3.8 : 1.0

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

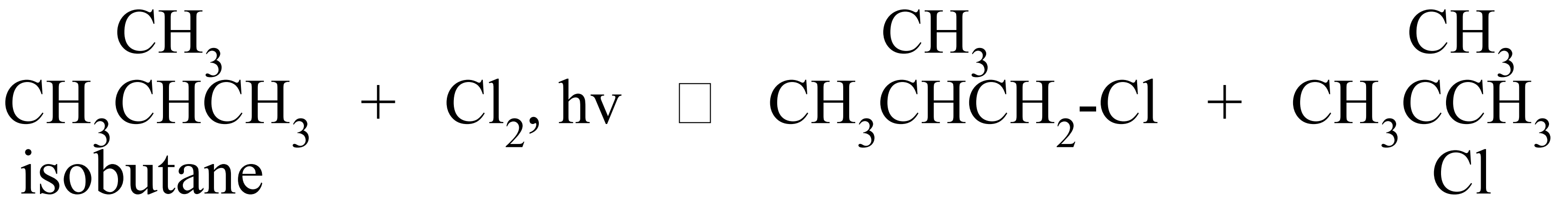


$$CH_3CH_2CH_2CH_3 \;+\; Cl_2,\ hv \;\rightarrow\; CH_3CH_2CH_2CH_2\text{-}Cl$$

n-butane

$$+\; CH_3CH_2\underset{Cl}{CH}CH_3$$

n-butyl chloride = (# of 1° hydrogens) x (reactivity of 1°)
= 6 x 1.0 = 6.0
sec-butyl chloride = (# of 2° hydrogens) x (reactivity of 2°)
= 4 x 3.8 = 15.2
% *n*-butyl chloride = 6.0/(6.0 + 15.2) x 100% = 28%
% *sec*-butyl chloride = 15.2/(6.0 + 15.2) x 100% = 72%



$$CH_3\overset{CH_3}{C}HCH_3 + Cl_2\text{, hv} \rightarrow CH_3\overset{CH_3}{C}HCH_2\text{-}Cl + CH_3\underset{Cl}{\overset{CH_3}{C}}CH_3$$

isobutane

isobutyl chloride = (# of 1° H's) x (reactivity of 1°)
= 9 x 1.0 = 9.0

tert-butyl chloride = (# of 3° H's) x (reactivity of 3°)
= 1 x 5.0 = 5.0

% isobutyl = (9.0/(9.0 + 5.0)) x 100% = 64%

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

Relative reactivity in bromination:

$3^{o} : 2^{o} : 1^{o} = 1600 : 82 : 1$

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

isobutane + Br_2, hv □ 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° > 2° > 1° ?

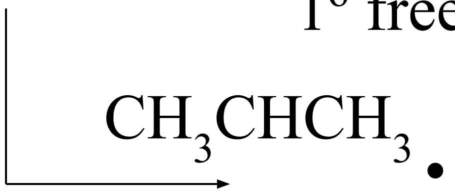
$CH_3\text{—}H$ □ $CH_3\bullet$ + $H\bullet$ $\Delta H = 104$ Kcal/mole

$CH_3CH_2\text{—}H$ □ $CH_3CH_2\bullet$ + $H\bullet$ $\Delta H = 98$ Kcal/mole

1° free radical

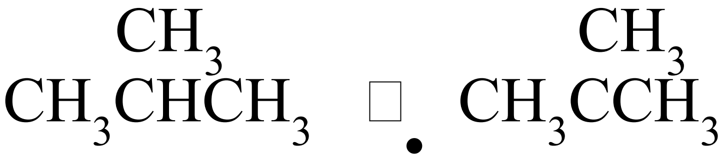
$CH_3CH_2CH_3$ □ $CH_3CH_2CH_2\bullet$ + $H\bullet$ $\Delta H = 98$ Kcal/mole

1° free radical



$CH_3\underset{\bullet}{C}HCH_3$ + $H\bullet$ $\Delta H = 95$ Kcal/mole

2° free radical



$CH_3\overset{CH_3}{C}HCH_3$ □ $CH_3\underset{\bullet}{\overset{CH_3}{C}}CH_3$ + $H\bullet$ $\Delta H = 92$ Kcal/mole

3° free radical

Relative reactivity in halogenation:

Stability of free radicals:

Ease of formation of free radicals:

Ease of abstraction of H's:

$3^{o} > 2^{o} > 1^{o} > CH_4$

1. Halogenation

R-H + X_2, heat or hv □ R-X + HX

a) heat or light required for reaction.

b) X_2: $Cl_2 > Br_2 \neq I_2$

c) yields **mixtures** ☹

d) H: $3^o > 2^o > 1^o > CH_4$

e) bromine is more selective

Alkane, reactions:

1. Halogenation

2. Combustion (oxidation)

3. Pyrolysis (cracking)