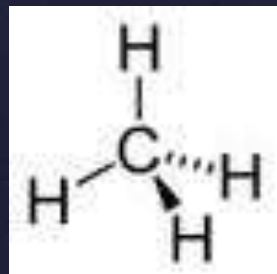
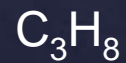
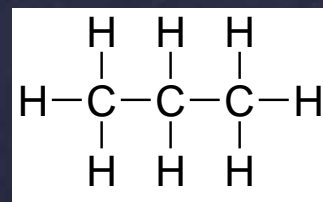
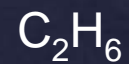
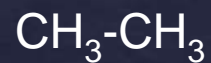
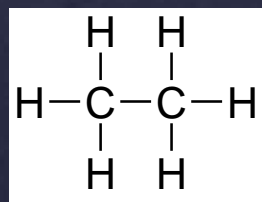
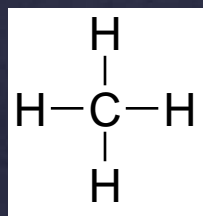




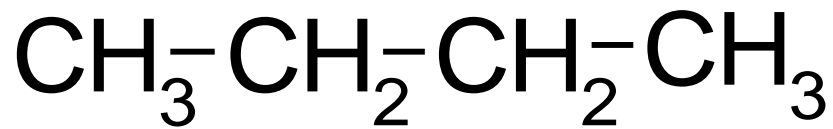
Marie Skłodowska Curie

Alkanes & IUPAC

Representation of Organic molecules



Structural isomers: same molecular formula, different compounds

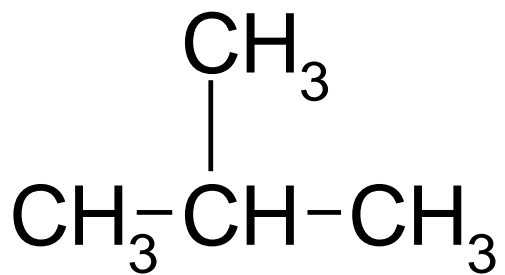


Butane



T melting Density

-0,5°C 0,579 g/mL



Isobutane



-11,6°C 0,549 g/mL

C_4H_{10} **Molecular formula**

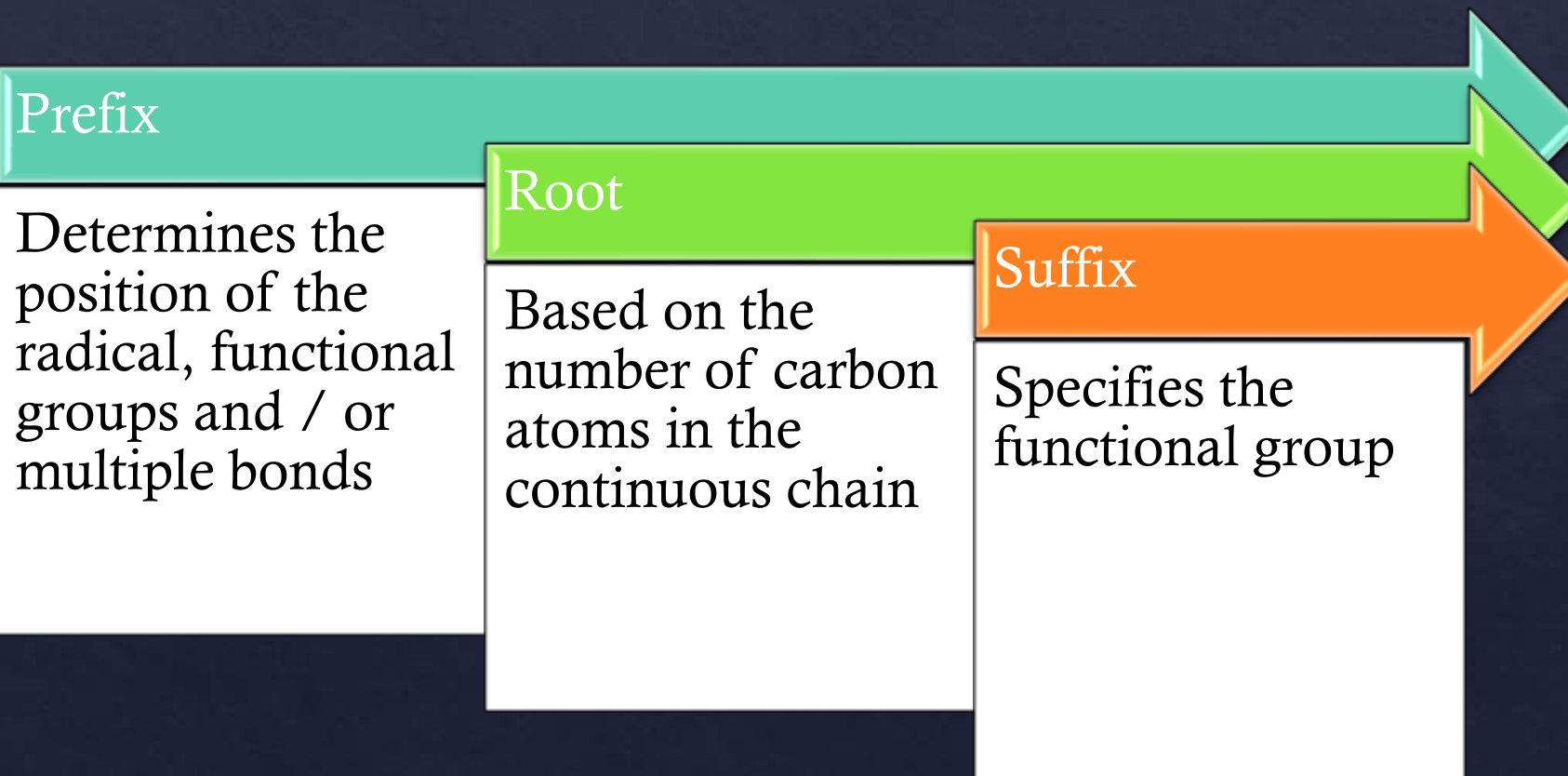
Nomenclature

International Union of Pure and Applied Chemistry (IUPAC)

The names prescribed by IUPAC are systematic, meaning that one name describes a specific compound and vice versa. We also use trivial names for compounds commonly found in everyday life (acetic acid, formic acid ...).



Nomenclature



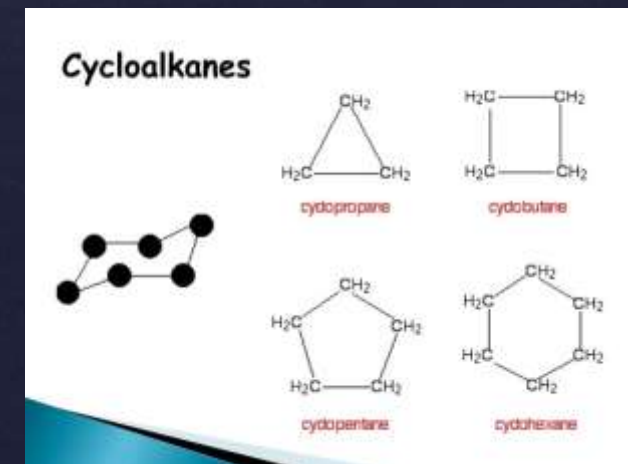
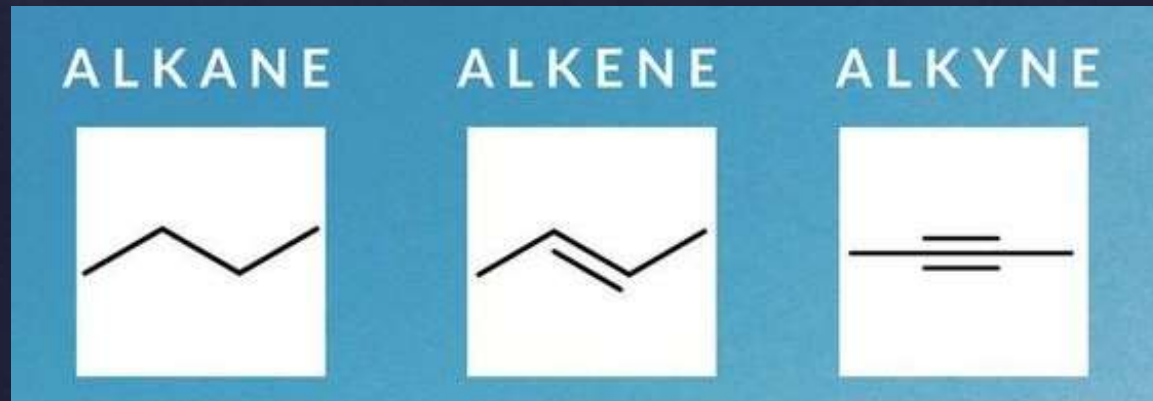
Functional groups

Are defined by subunits and bonds that determine their chemical reactivity



Example of nomenclature

- ◇ **ALK** (root) **ANE** (suffix saying there are only single bonds between carbon atoms)
- ◇ **ALK** (root) **ENE** (suffix saying there is a double bond)
- ◇ **ALK** (root) **YNE** (suffix saying there is a triple bond)
- ◇ **CYCLO** (prefix) **ALK** (root) **ANE** (suffix saying there are only single bonds between carbon atoms)

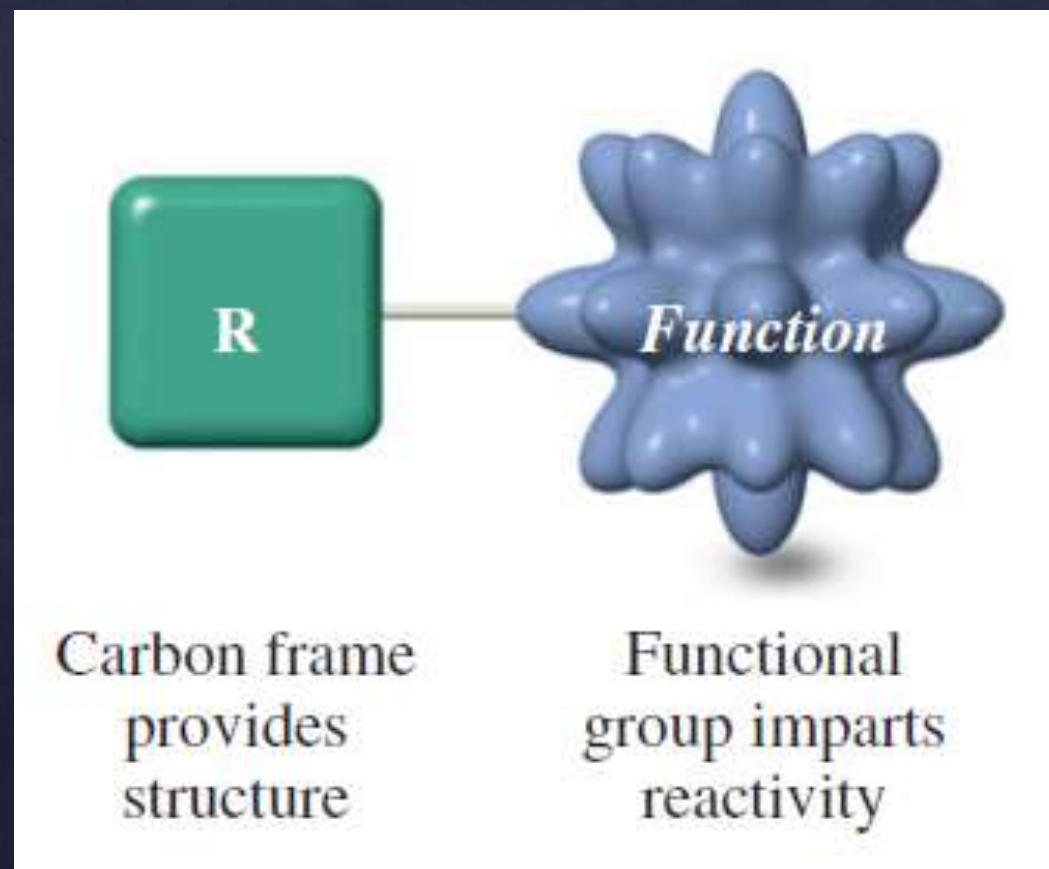


Nomenclature



Name	Formula	Suffix/Prefix
Carboxylic Acids	-COOH	-oic acid
Esters	-COOR	-oate
Halogenoid Acids	-COX	Chloro-/Bromo- etc.
Amides	-CONH ₂	-ide
Nitriles	-CN	Cyano-
Aldehydes	-CHO	-al
Ketones	-CO-	-one
Alcohols	-OH	-ol
Phenols	-OH	Pheno(l)-
Amines	-NH ₂	-amine
Ethers	-OR	-ethane

Why are functional groups mentioned in the name?

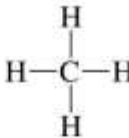

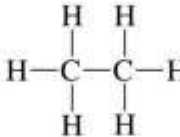
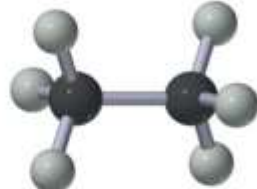
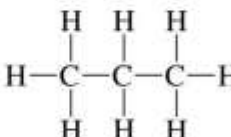
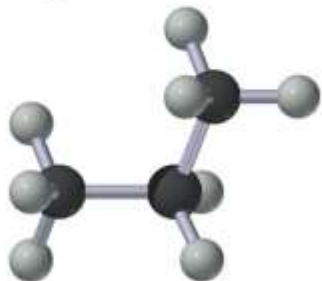
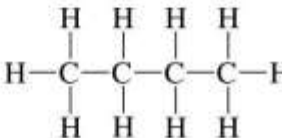
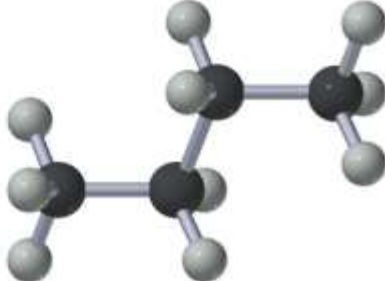


Alkane

Alkane are simple **hydrocarbons**, they only have single bonds, no functional group and their molecular formula is C_nH_{2n+2}

- Relatively **nonpolar**
- Relatively **unreactive**

They can be in circular form (**Cycloalkanes**)

name	Kekulé structure	condensed structure	ball-and-stick model
<u>methane</u>		CH ₄	
<u>ethane</u>		CH ₃ CH ₃	
<u>propane</u>		CH ₃ CH ₂ CH ₃	
<u>butane</u>		CH ₃ CH ₂ CH ₂ CH ₃	

Picture by 1840460mahesh via Wikimedia Commons

Alkane

Molecular formula	Name	T boiling [°C]	T melting [°C]
CH ₄	Methane	-164	-182
C ₂ H ₆	Ethane	-89	-183
C ₃ H ₈	Propane	-42	-190
C ₄ H ₁₀	Butane	0	-138
C ₅ H ₁₂	Pentane	36	-130
C ₆ H ₁₄	Hexane	69	-95
C ₇ H ₁₆	Heptane	98	-91
C ₈ H ₁₈	Octane	126	-57
C ₉ H ₂₀	Nonane	151	-51
C ₁₀ H ₂₂	Decane	174	-30

Alkanes

Hydrocarbons without functional groups

Straight chain: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

Line notation:

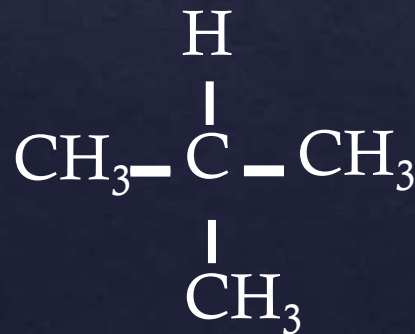


Butane

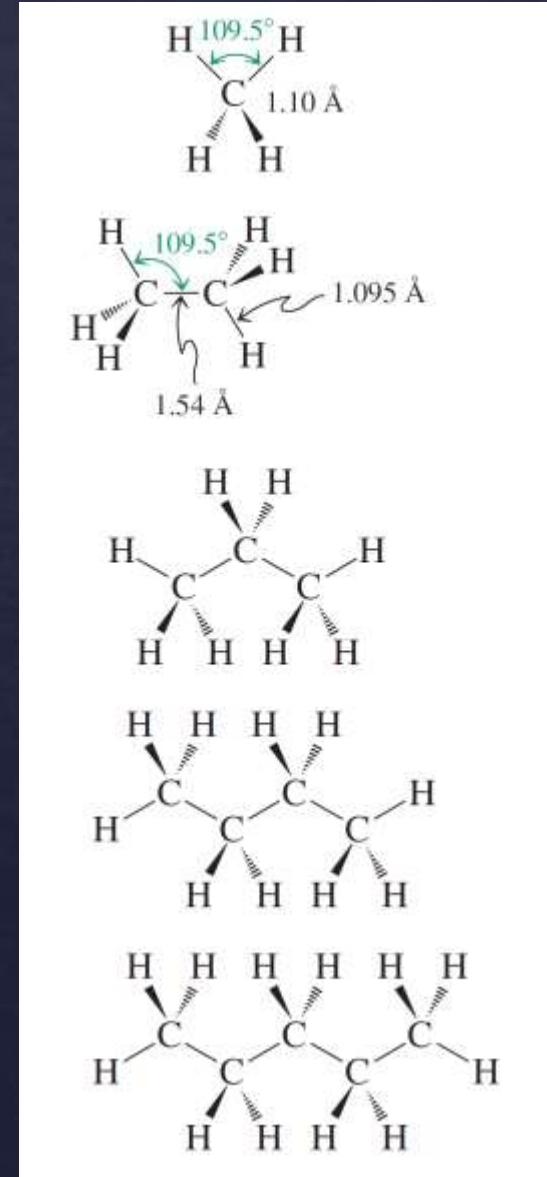
Branched:



2-Methylpropane
(Isobutane)



$$1 \text{ \AA} = 10^{-8} \text{ cm}$$



Homologous Series

Insert $-\text{CH}_2-$ groups into C-C bonds.

Straight chain $\text{CH}_3(\text{CH}_2)_x\text{CH}_3$

General molecular formula
for acyclic systems.

Cyclic alkanes: C_nH_{2n}

Table

2.4

Number of
Possible
Isomeric
Alkanes,
 $\text{C}_n\text{H}_{2n+2}$

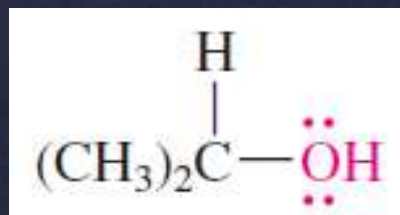
n	Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319

What about functional groups?



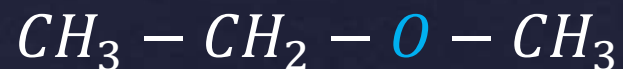
Haloalkanes

Bromoethane



Alcohols

2-Propanol



Ethers

Methoxyethane



Thiols

Ethanethiol

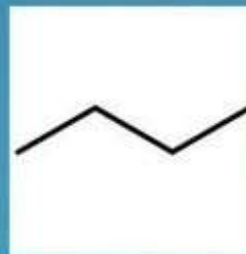


Alkenes and Alkynes

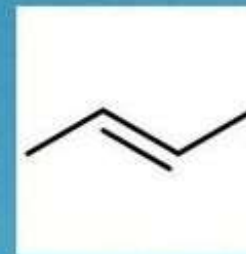
Alkane Name	Alkene name	Alkyne name
Methane	-	-
Ethane	Ethene	Ethyne
Propane	Propene	Propyne
Butane	Butene	Butyne
Pentane	Pentene	Pentyne
Hexane	Hexene	Hexyne
Heptane	Heptene	Heptyne
Octane	Octene	Octyne
Nonane	Nonene	Nonyne
Decane	Decene	Decyne



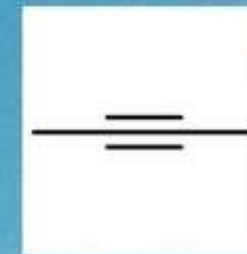
ALKANE



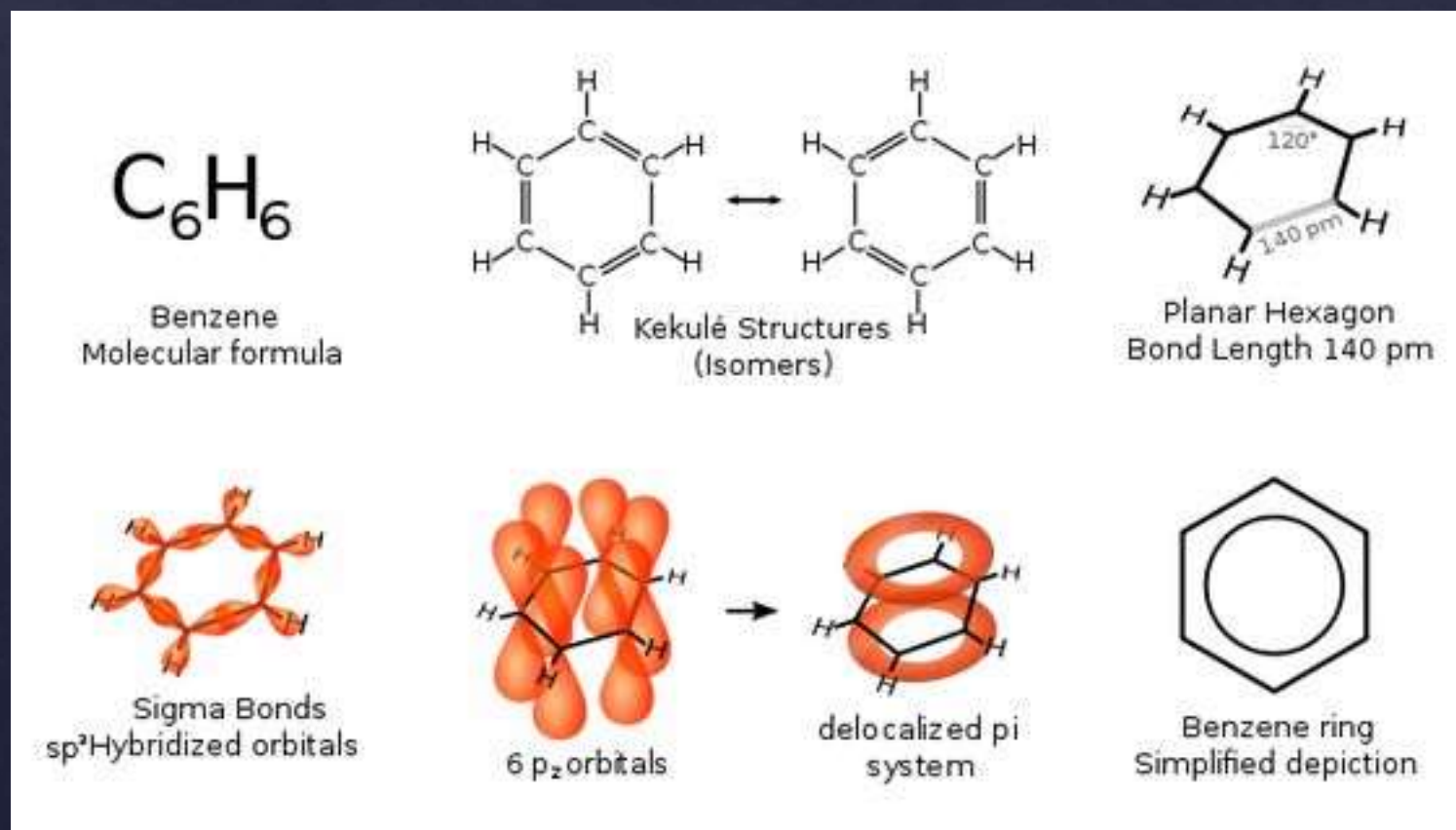
ALKENE



ALKYNE



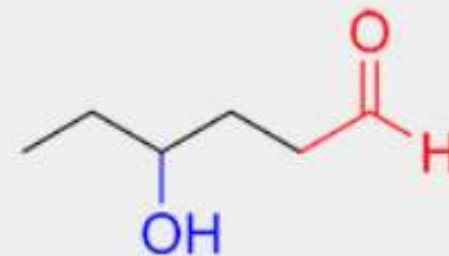
Alkenes and aromatic compounds (Arenes)



Nomenclature, step by step

Step 1

Determine the primary functional group



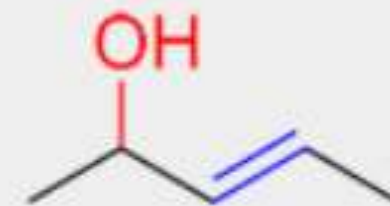
If more than one, set priority

- Usually the most oxidized has highest priority (will be suffix, others will be prefix)

Suffix: -al
Prefix: hydroxy-

Alkene & Alkyne cannot be prefix

- If higher priority groups are present: root -en/-yn - suffix

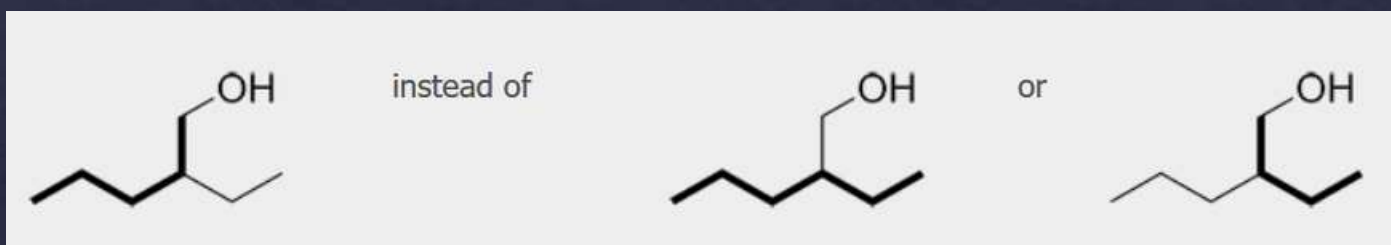


-enol

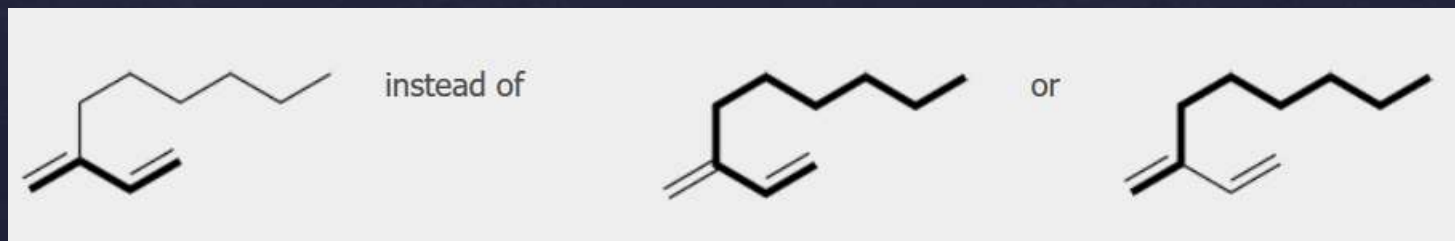
Nomenclature, step by step

Step 2

Determine the primary carbon chain which contains the primary functional group.



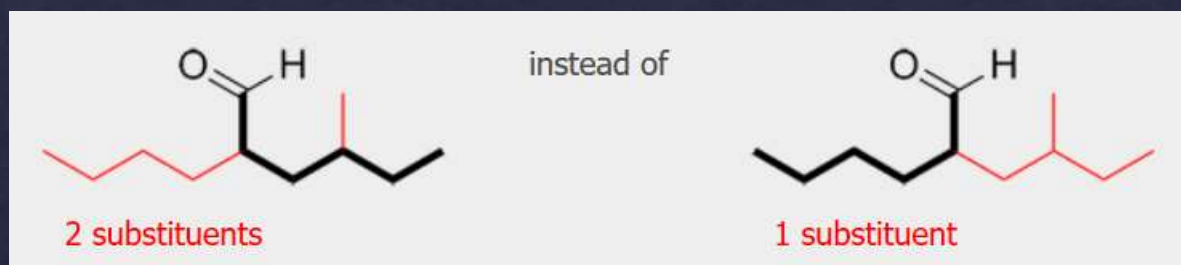
If there is more than one option, choose the chain with the maximum number of multiple bonds



Nomenclature, step by step

Step 2

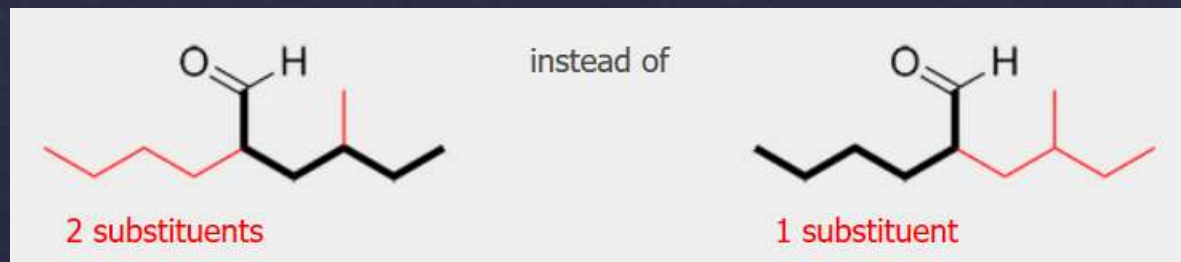
If there are two chains of the same length, choose the one with the maximum number of substituents



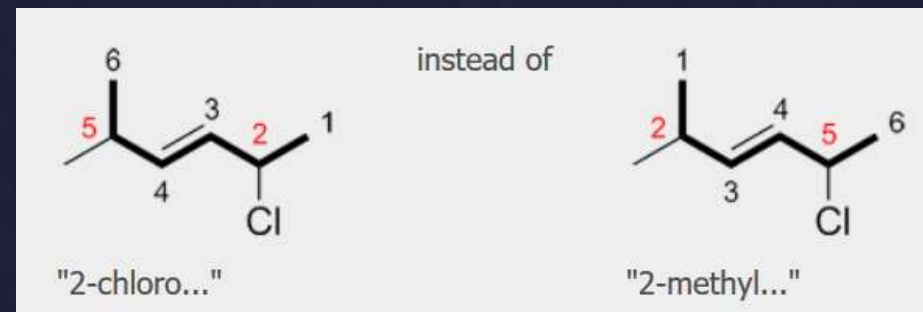
Nomenclature, step by step

Step 3

If there are two chains of the same length, choose the one with the maximum number of substituents

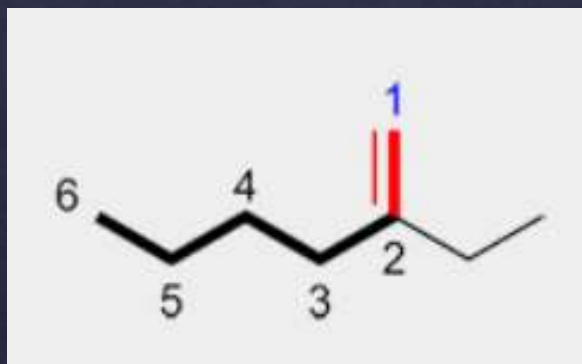


Carbons should be numbered so that the primary functional group has the lowest possible number. If it's the same, then number it so that other substituents also have the lowest possible number. If it's the same, then number the chain so the first substituent in alphabetical order has the smaller number



Nomenclature, step by step

Step 4



6 carbons
Alkene



hex-
-ene

Now the substituent
Alkane
2 carbons
On 2nd carbon



-yl
Eth-
2-ethyl





I U P A C

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

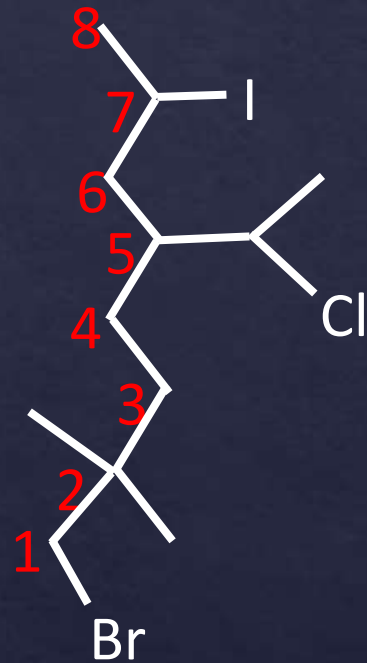


Longest chain?

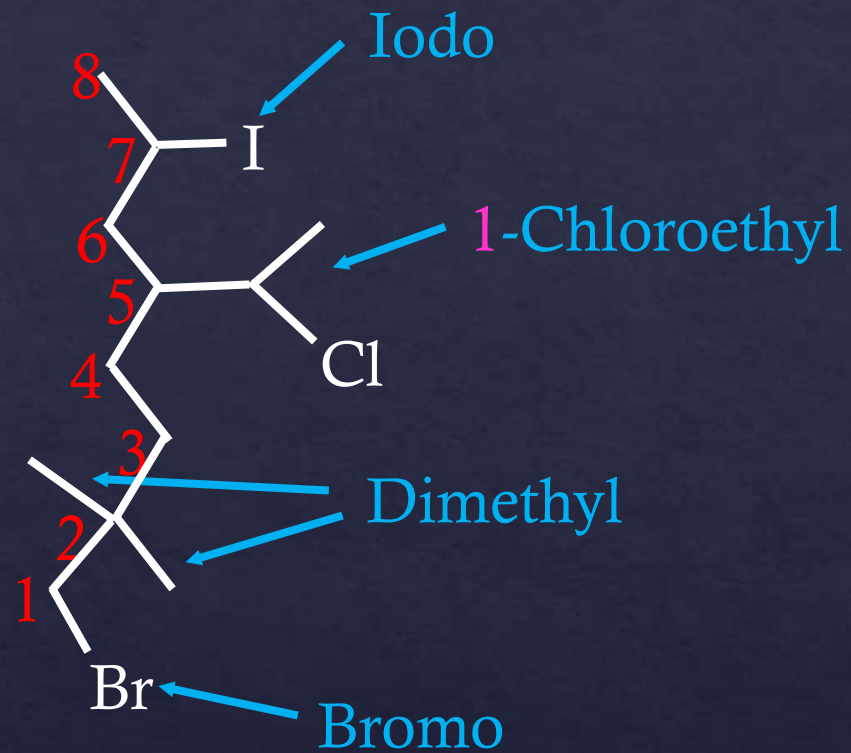


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Substituents?

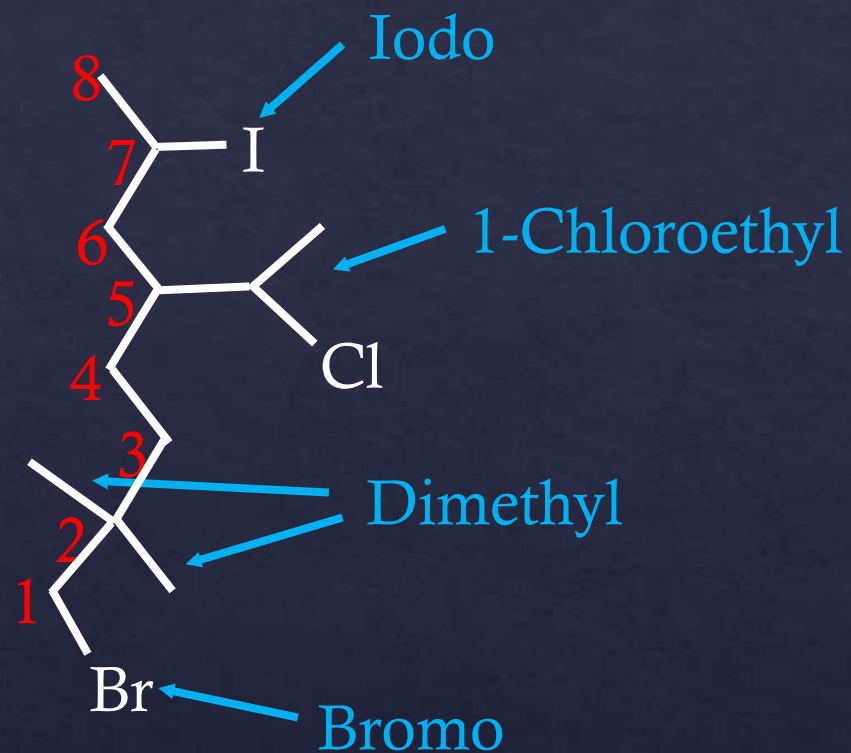


Final name? We proceed alphabetically



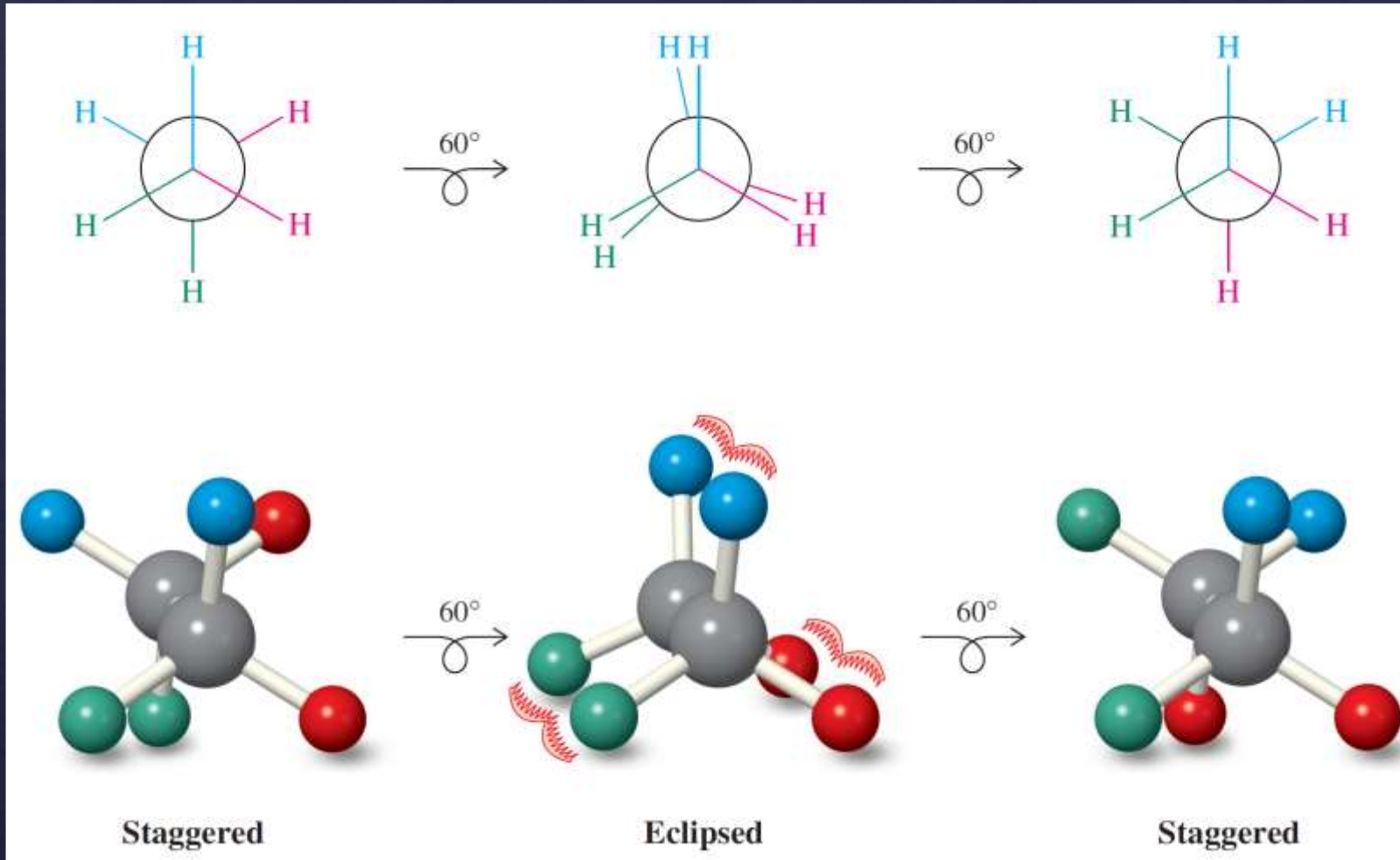
I U P A C

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1-Bromo-5-(1-chloroethyl)-7-iodo-2,2-dimethyloctane

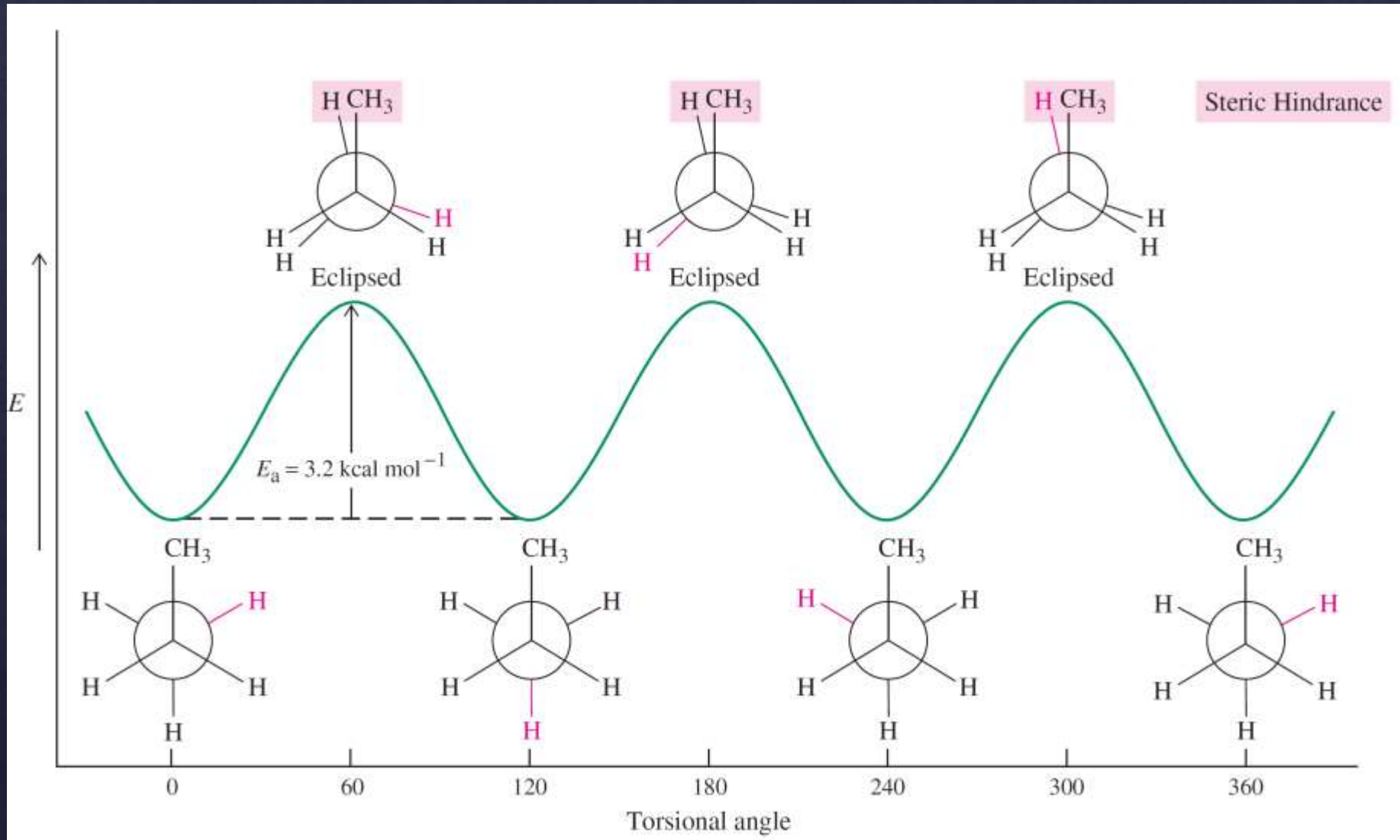
Rotation with Newman projections



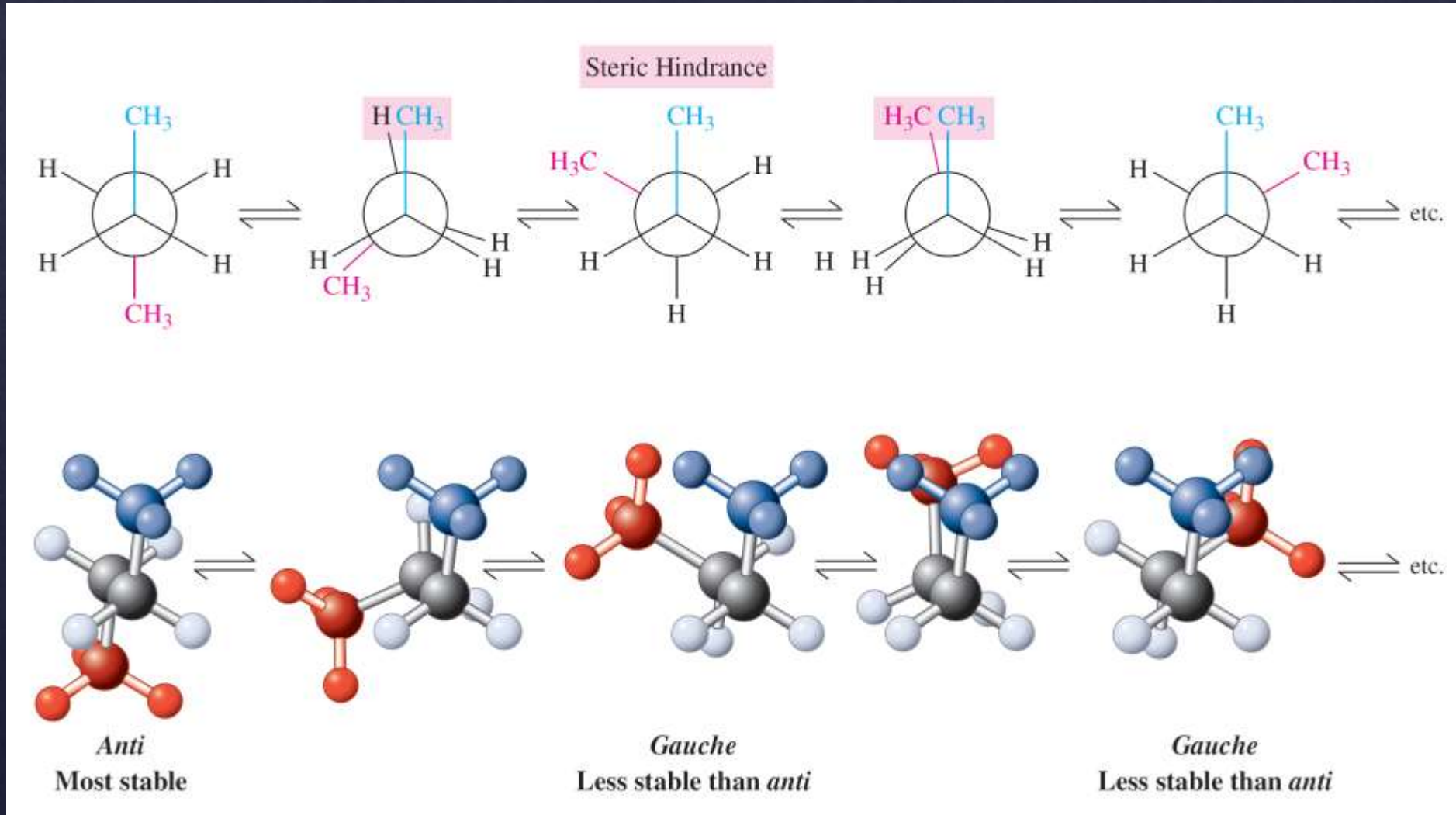
Most stable

Higher energy

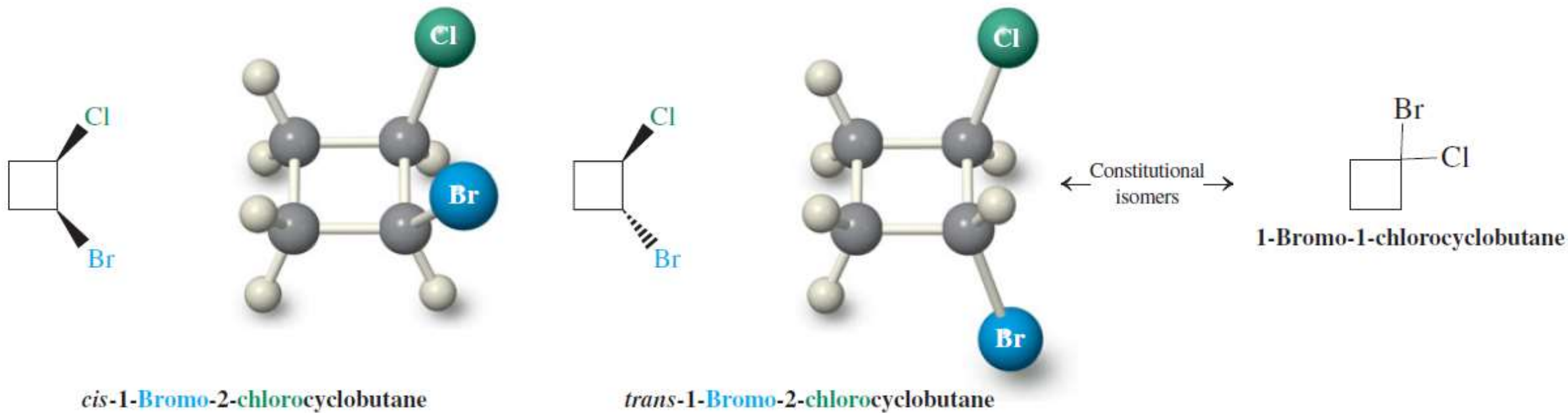
Steric hindrance



Isomeric Rotamers – with increasing complexity the number of conformations increases too



However...



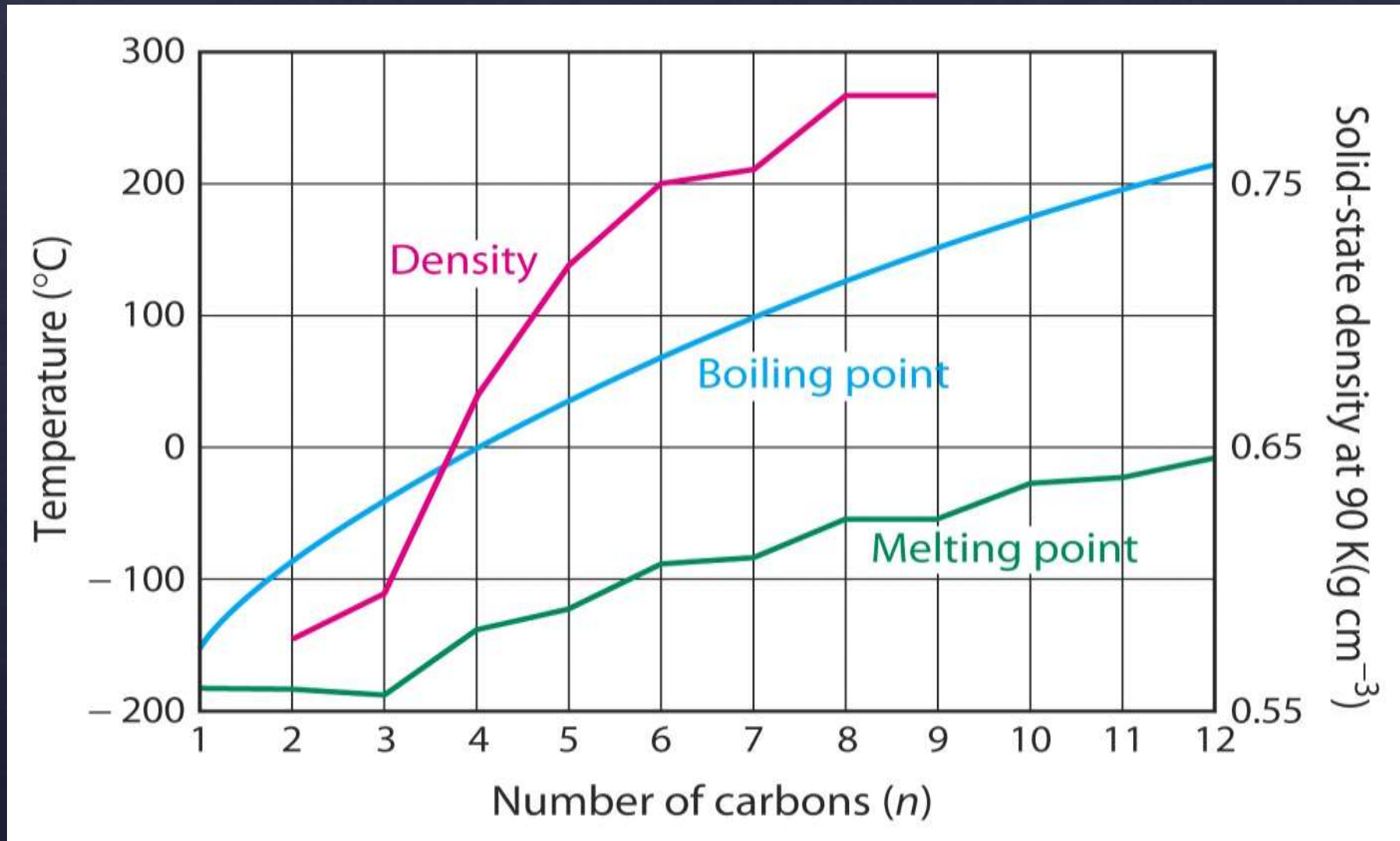
Picture from Vollhardt & Schore

The stereoisomers have the same molecular and structural formula and a different three-dimensional structure.

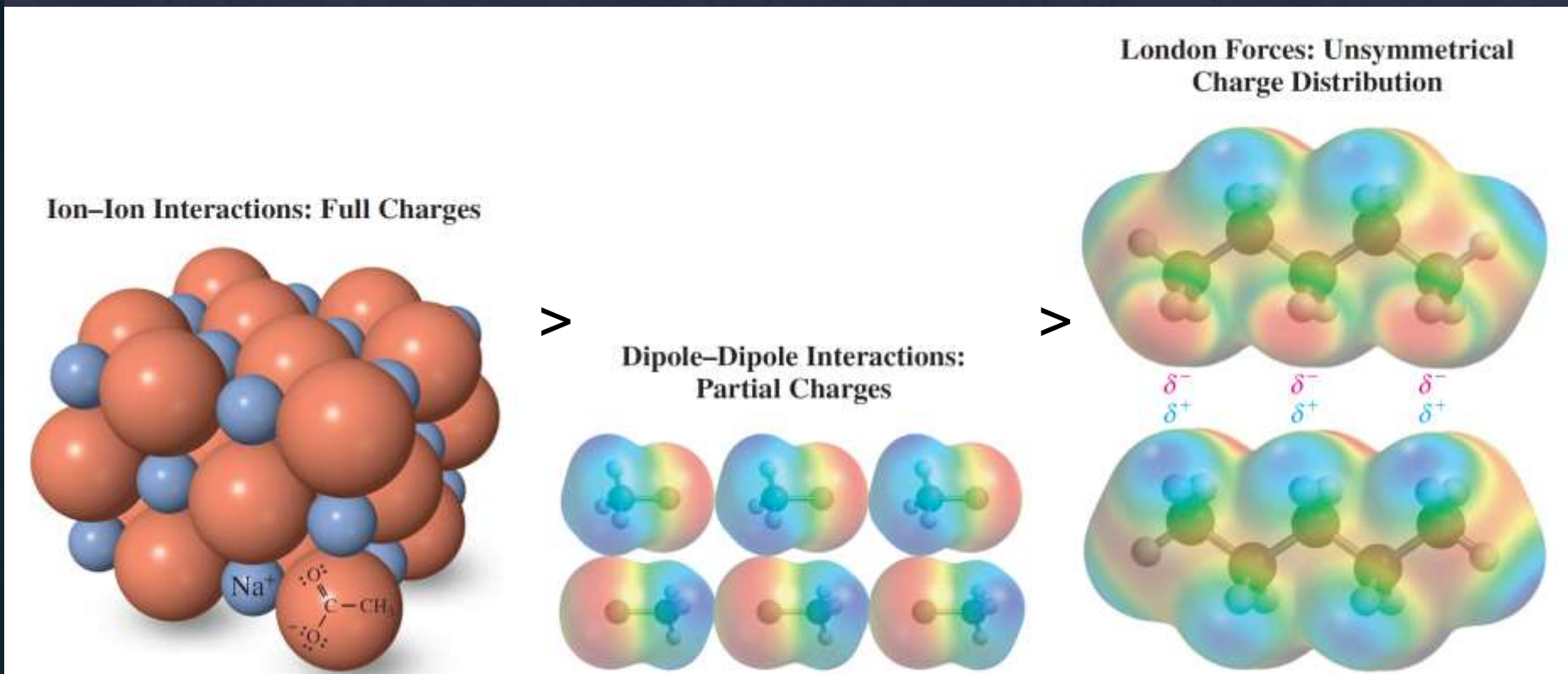
Switching from one shape to another is only possible when the ring is opened. Both isomers have different properties (T boiling).

Physical Properties Of Alkanes

Intermolecular Forces Increase With Size



Intermolecular Forces



Salts

Polar molecules

Alkanes (alkyls)

Natural alkanes and alkenes

Pheromones

A complex mixture of alkanes and alkenes, containing different numbers carbon atoms (>20) depending on the species.

The fragrance of this mixture attracts sexual partners, but is also mimicked by some plants for pollination purposes.





Reactions

Combustion



$\Delta H^\circ_{\text{comb}}$ \uparrow with \uparrow length of C-chain

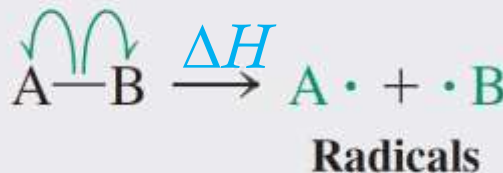
Isomeric alkanes **don't** have the same $\Delta H^\circ_{\text{comb}}$



Radical halogenation and bond strength

Reactions require bond breaking and bond making

Bond strengths:
homolytic cleavage



$\Delta H = DH^\circ =$ Bond dissociation energy (kcal mol^{-1})

This process contrasts with heterolytic cleavage



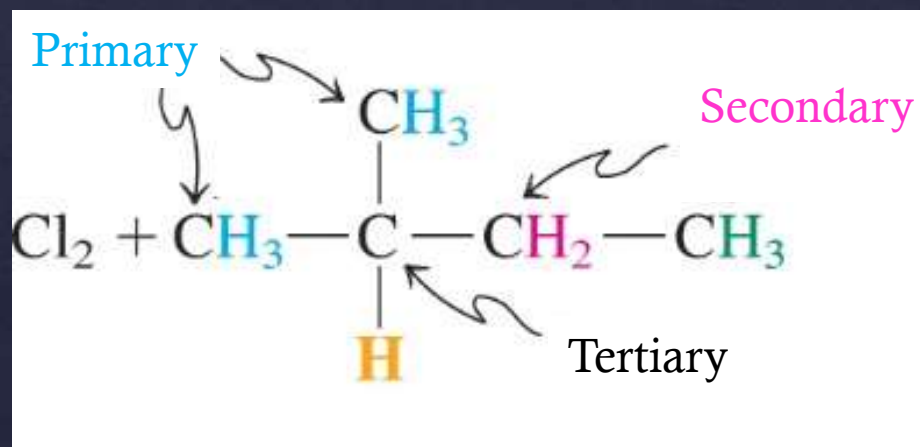
For example: $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

but $\text{H}-\text{OH}$, $DH^\circ = +119$

C-H Bond Strengths

To functionalize alkanes, we need to break C-H

But: Are all C-H bonds the same ?



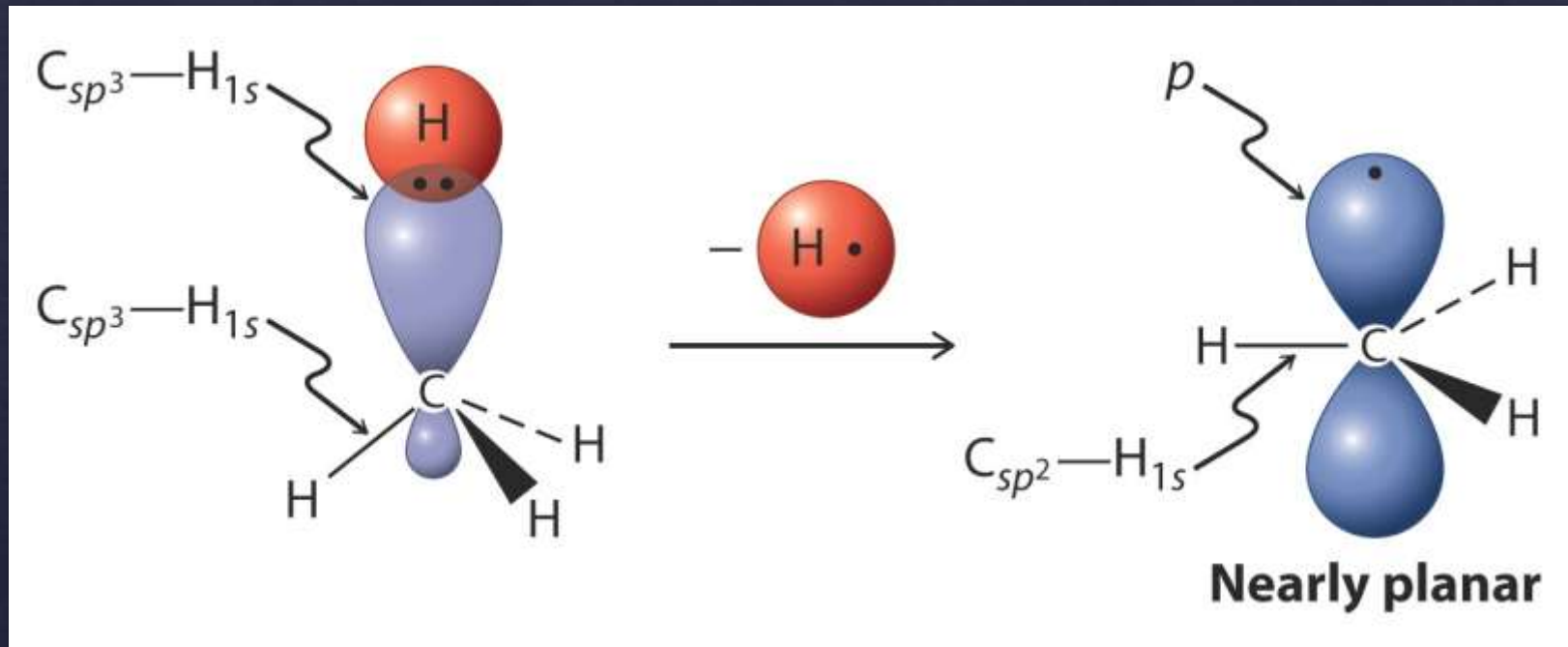
→ No!

DH° s decrease along the series:



Structure of alkyl radicals

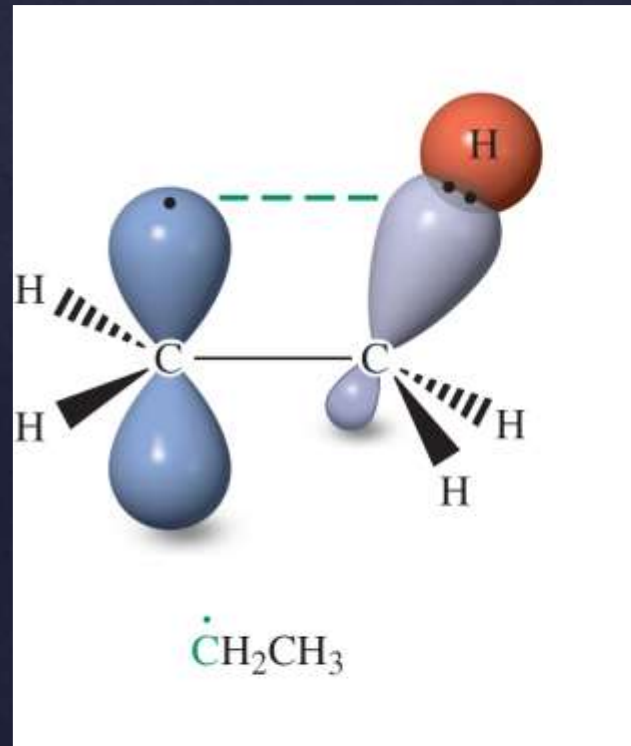
R^\bullet is sp^2 -hybridized.



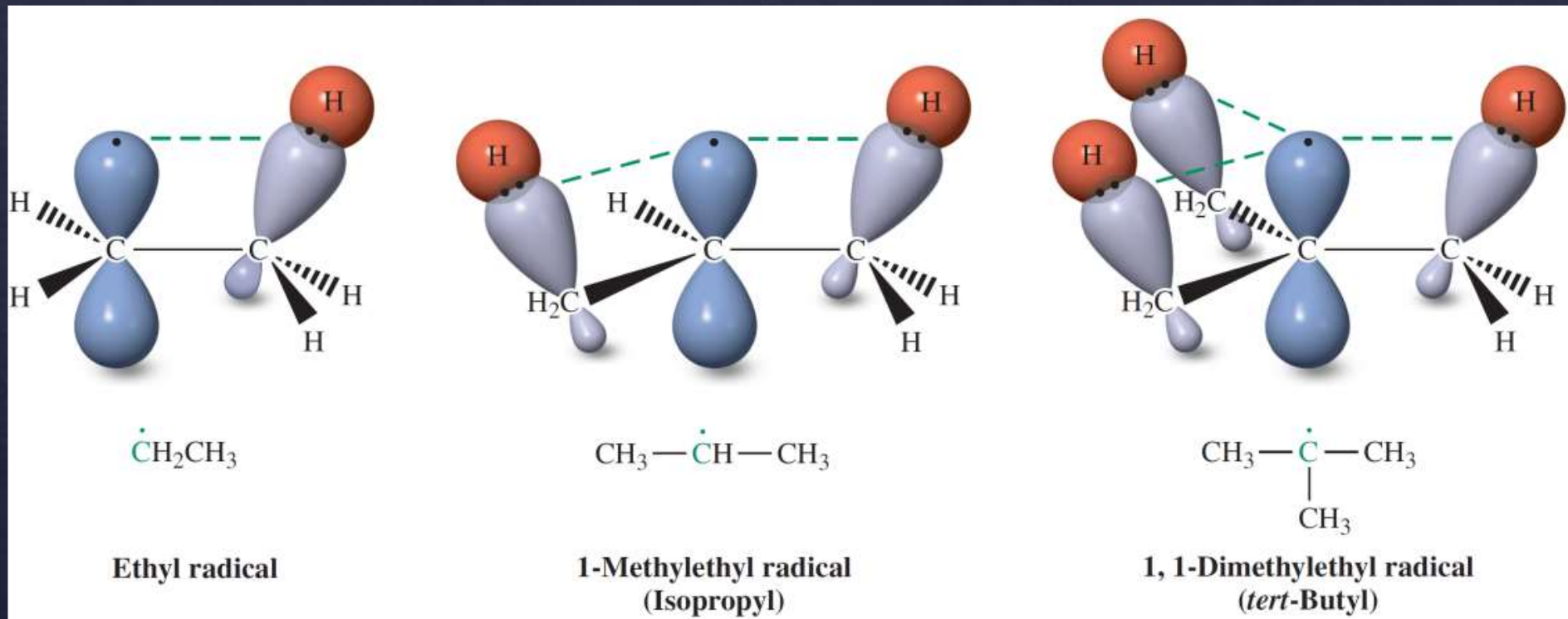
Substitution stabilizes the radical. How?

Hyperconjugation

p-Orbital (with single e) overlaps with bonding molecular orbital of neighboring C-H (or any other) bond.



More neighboring bonds: more hyperconjugation



Prediction: The more substituted C-H should be more reactive

Pyrolysis

Breaking longer carbon-chains into shorter ones

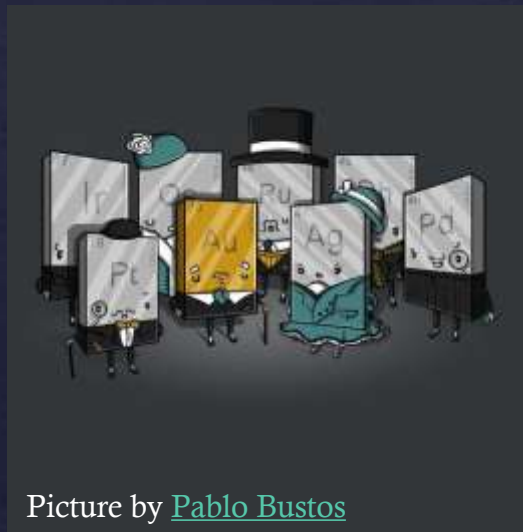
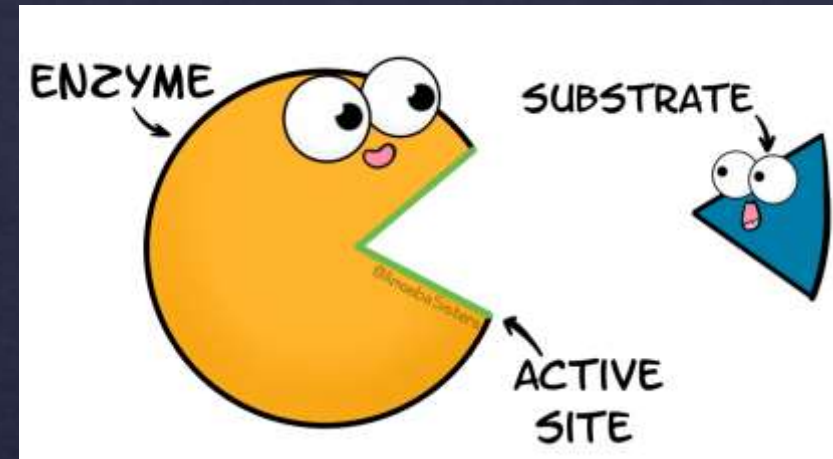
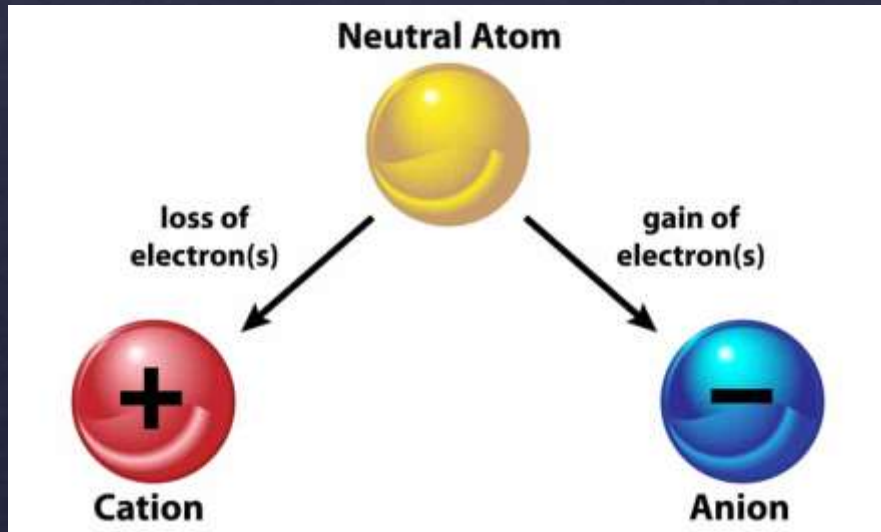


T



Selectivity

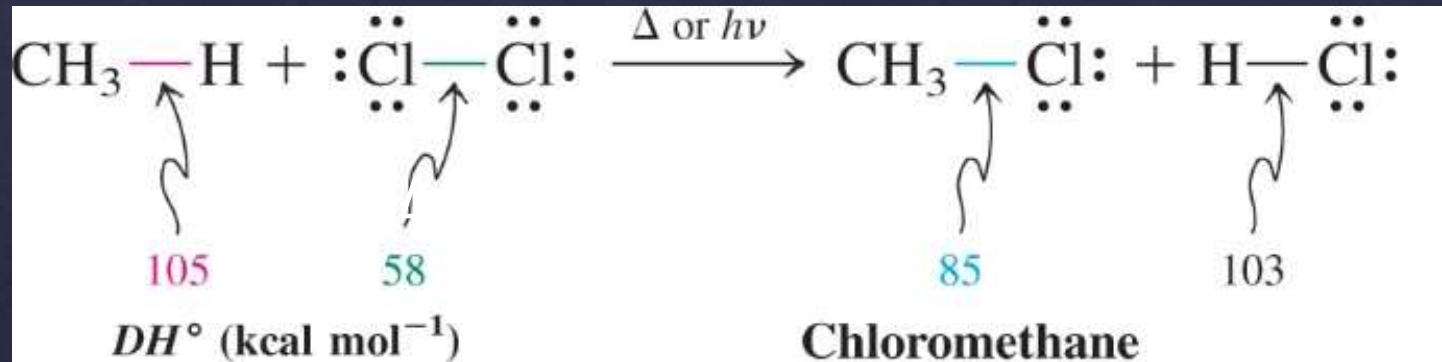
Catalyst



Picture by [Pablo Bustos](#)

Radical Halogenation: Methane And Chlorine (Kcal Mol⁻¹)

163

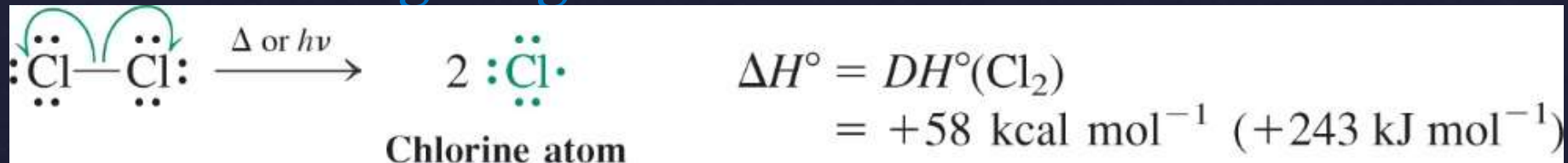


188

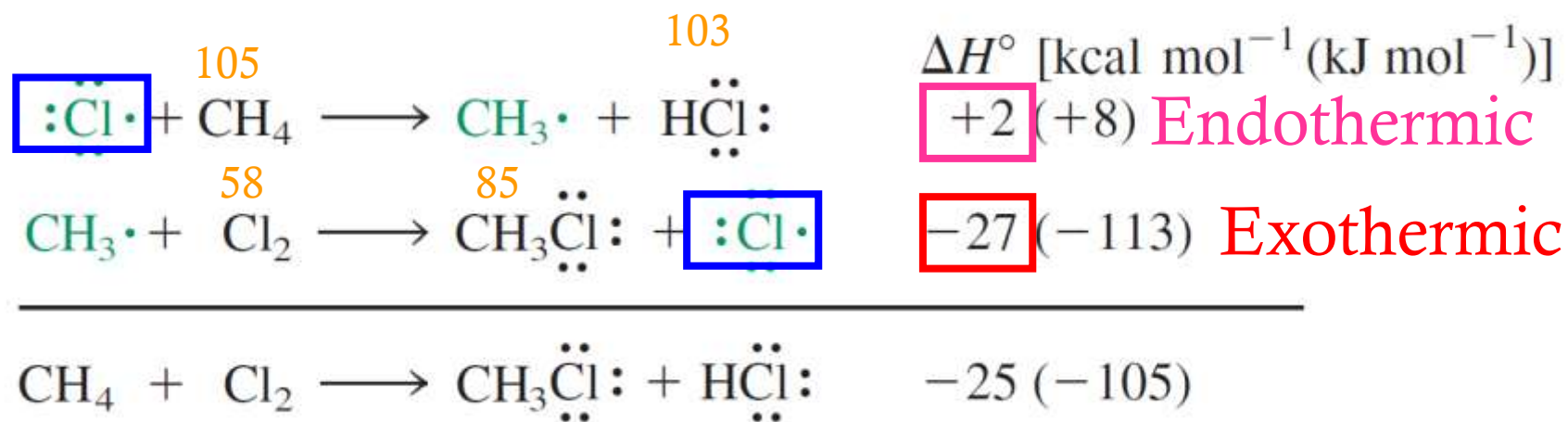
Exothermic, but needs heat (Δ) (300°C) and/or (UV)light to start.

Mechanism

1. Initiation: “lighting the match”



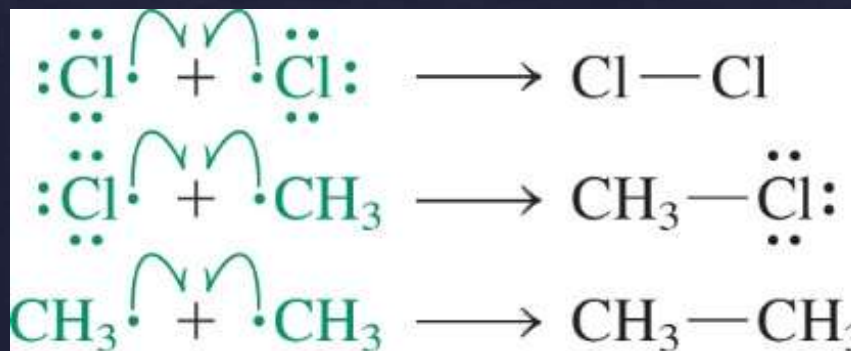
2. Propagation (“fire”): A radical chain mechanism



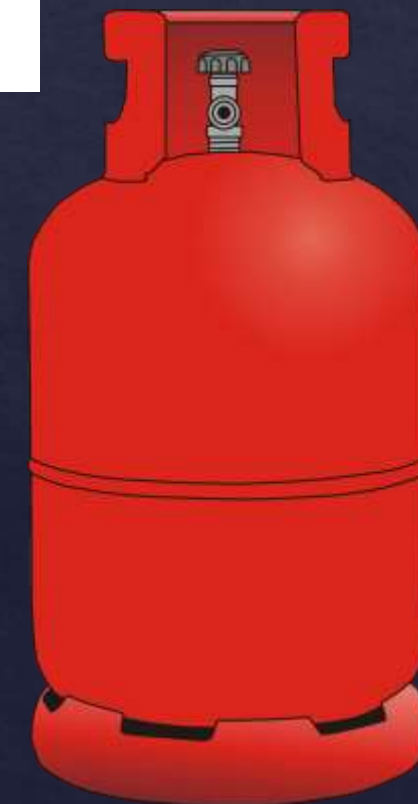
Note: Initiation step **does not enter** into equation. Only a few $\text{Cl}\cdot$ needed to convert all of the starting material.

3. Termination:

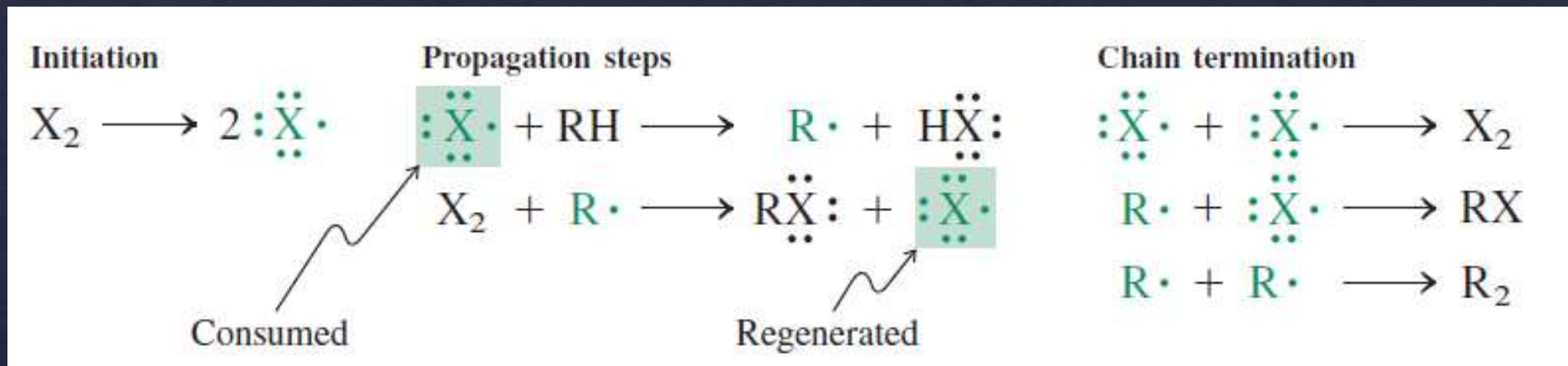
Kills
propagation



Pictures from Vollhardt & Schore



Radical chain mechanism



Picture from Vollhardt & Schore



Write a detailed mechanism for the light-initiated monochlorination of ethane, which furnishes chloroethane. Calculate ΔH° for each step.

Begin by writing the overall equation for the reaction and calculating its ΔH° , using data in these tables and the formula $\Delta H^\circ = \sum \Delta H^\circ$ (bonds broken) - $\sum \Delta H^\circ$ (bonds formed). Then write the initiation, propagation, and termination steps for a typical radical chain mechanism.

Table 3-1 Bond-Dissociation Energies of Various A–B Bonds in the Gas Phase [DH° in kcal mol⁻¹ (kJ mol⁻¹)]

A in A–B	B in A–B						
	–H	–F	–Cl	–Br	–I	–OH	–NH ₂
H—	104 (435)	136 (569)	103 (431)	87 (364)	71 (297)	119 (498)	108 (452)
CH ₃ —	105 (439)	110 (460)	85 (356)	70 (293)	57 (238)	93 (389)	84 (352)
CH ₃ CH ₂ —	101 (423)	111 (464)	84 (352)	70 (293)	56 (234)	94 (393)	85 (356)
CH ₃ CH ₂ CH ₂ —	101 (423)	110 (460)	85 (356)	70 (293)	56 (234)	92 (385)	84 (352)
(CH ₃) ₂ CH—	98.5 (412)	111 (464)	84 (352)	71 (297)	56 (234)	96 (402)	86 (360)
(CH ₃) ₃ C—	96.5 (404)	110 (460)	85 (356)	71 (297)	55 (230)	96 (402)	85 (356)

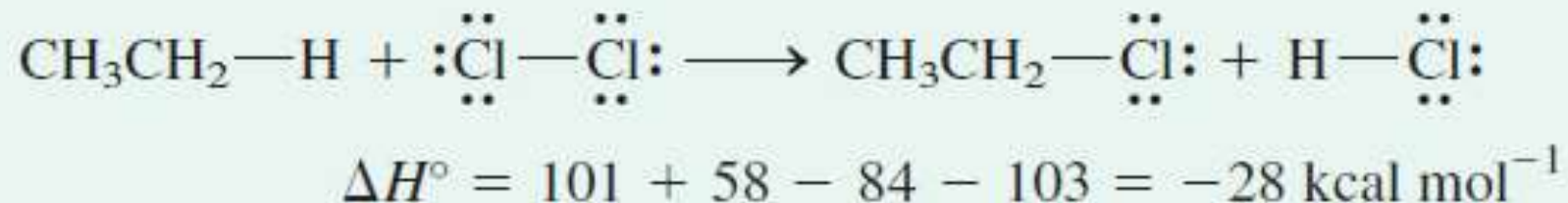
Note: (a) $DH^\circ = \Delta H^\circ$ for the process A–B → A· + ·B. (b) These numbers are being revised continually because of improved methods for their measurement. (c) The trends observed for A–H bonds are significantly altered for polar A–B bonds because of dipolar contributions to DH° .

Table 3-3 Product Distribution in a Typical Distillation of Crude Petroleum

Amount (% of volume)	Boiling point (°C)	Carbon atoms	Products
1–2	<30	C ₁ –C ₄	Natural gas, methane, propane, butane, liquefied petroleum gas (LPG)
15–30	30–200	C ₄ –C ₁₂	Petroleum ether (C _{5,6}), ligroin (C ₇), naphtha, straight-run gasoline ^a
5–20	200–300	C ₁₂ –C ₁₅	Kerosene, heater oil
10–40	300–400	C ₁₅ –C ₂₅	Gas oil, diesel fuel, lubricating oil, waxes, asphalt
8–69	>400 (Nonvolatiles)	>C ₂₅	Residual oil, paraffin waxes, asphalt (tar)

^aThis refers to gasoline straight from petroleum, without having been treated in any way.

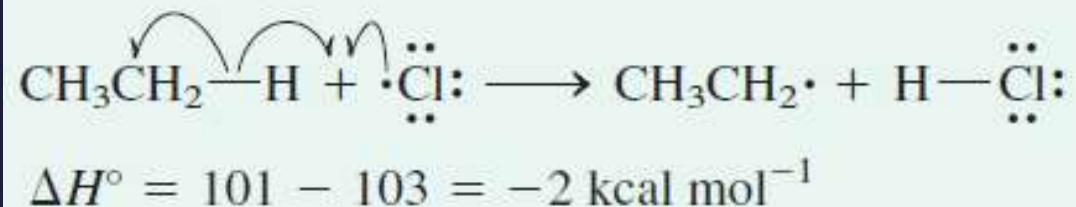
Overall equation:



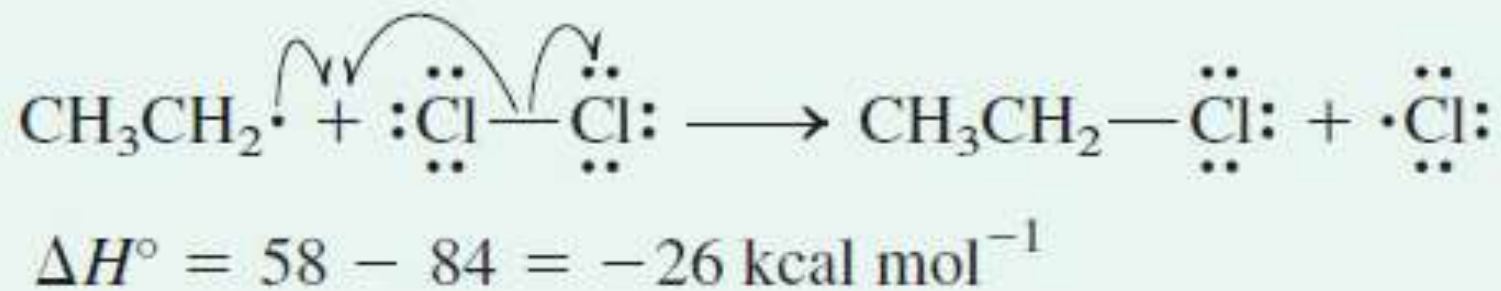
Initiation:



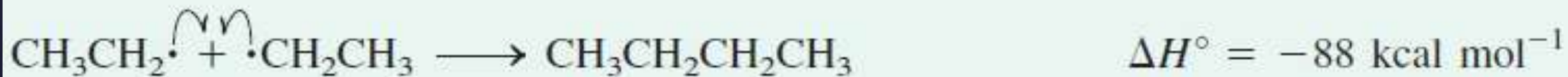
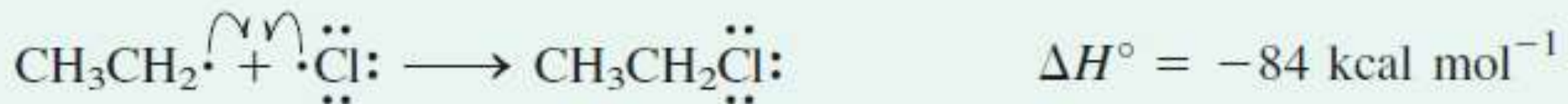
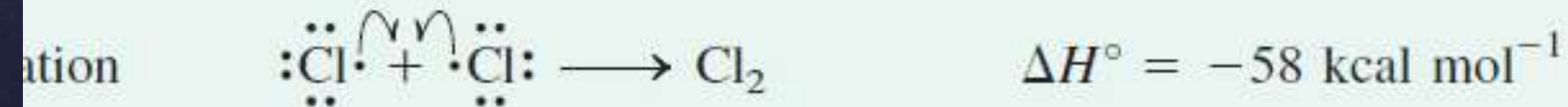
Propagation step1:



Propagation step2:



Termination:



Other halogenations of methane

Compare important ΔH° values:



F_2	Cl_2	Br_2	I_2	HF	HCl	HBr	HI	F	Cl	Br	I
38	58	46	36	136	103	87	71	110	85	70	57

Initiation OK for all

Reactivity: $\text{F}_2 > \underbrace{\text{Cl}_2 \sim \text{Br}_2}_{\text{good!}} > \cancel{\text{I}_2}$ Nope

F_2 explodes

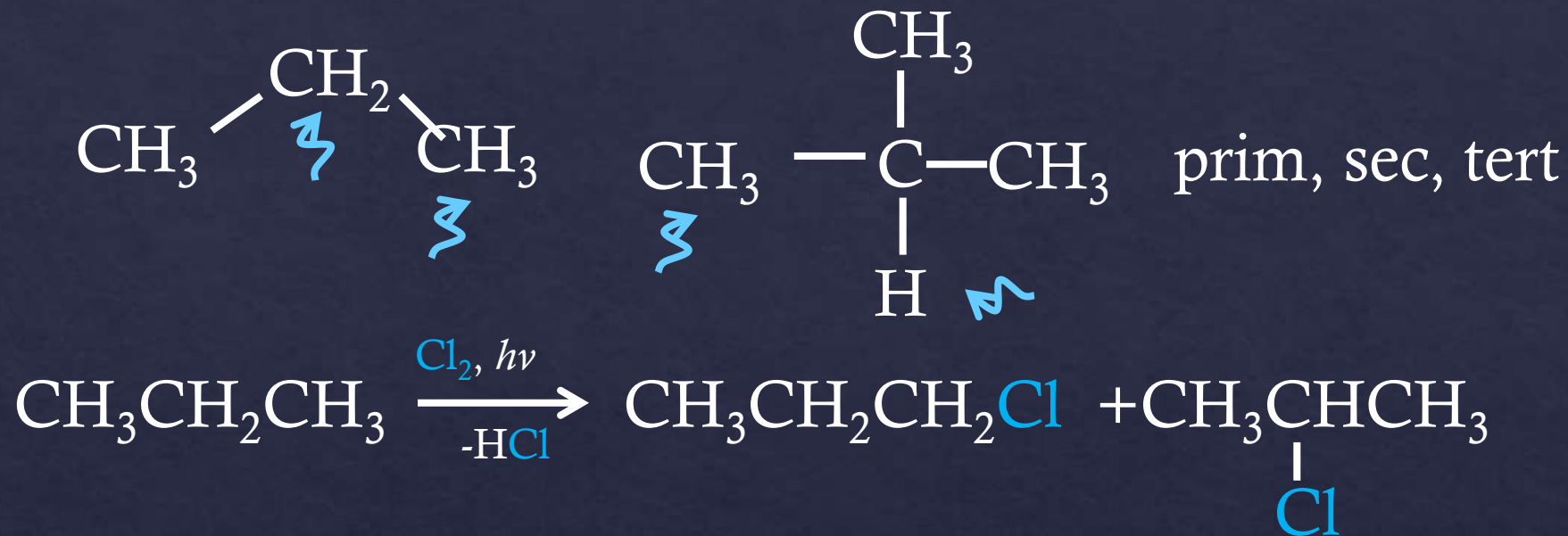
Cl_2 faster than Br_2

Table 3.5 Enthalpies of the Propagation Steps in the Halogenation of Methane [kcal mol⁻¹ (kJ mol⁻¹)]

Reaction	F	Cl	Br	I
Propagation step 1: $\cdot\ddot{\text{X}} + \text{CH}_4 \longrightarrow \cdot\text{CH}_3 + \text{H}\ddot{\text{X}}$	-31 (-130)	+2 (+8)	+18 (+75)	+34 (+142)
Propagation step 2: $\cdot\text{CH}_3 + \text{X}_2 \longrightarrow \text{CH}_3\ddot{\text{X}} + \cdot\ddot{\text{X}}$	-72 (-301)	-27 (-113)	-24 (-100)	-21 (-88)
Overall reaction: $\text{CH}_4 + \text{X}_2 \longrightarrow \text{CH}_3\ddot{\text{X}} + \text{H}\ddot{\text{X}}$	-103 (-431)	-25 (-105)	-6 (-25)	+13 (+54)

Endothermic

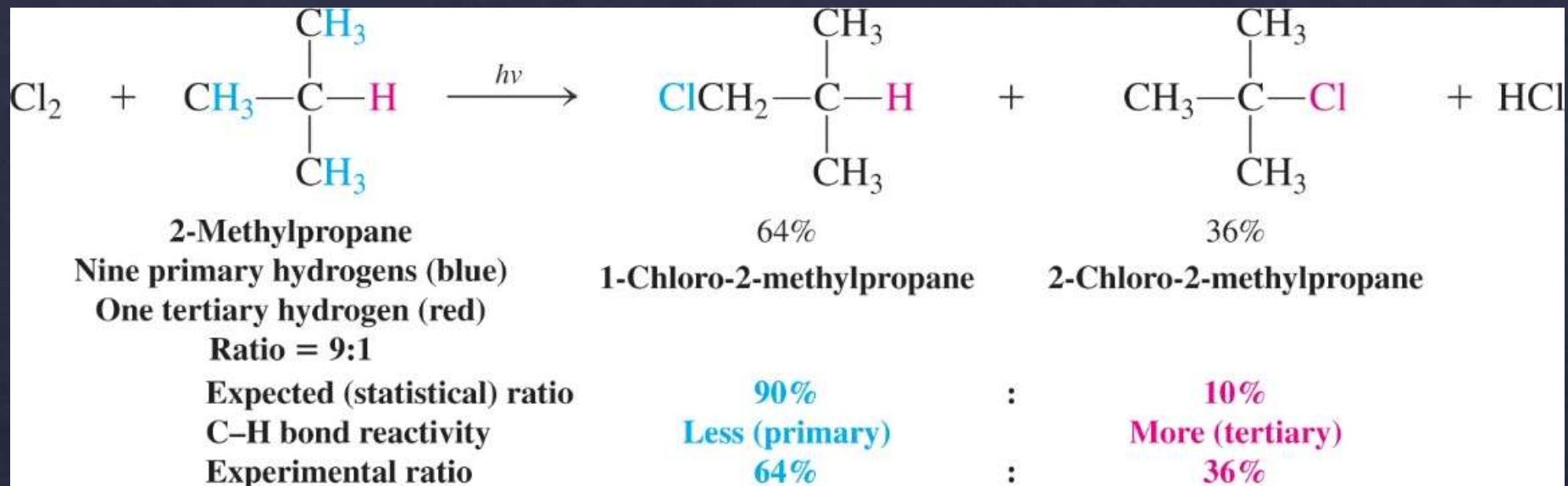
Selectivity for different C-H bonds



Statistical (expected)	3	:	1
$\text{R}-\text{H}$ (expected)	Less (prim)		More (sec)
Found (25 °C) :	43	:	57
Reactivity per H:	$43/6 = 7.2$		$57/2 = 28.5$
	1	:	4

Secondary C-H is more reactive than primary C-H

What about tertiary C-H?

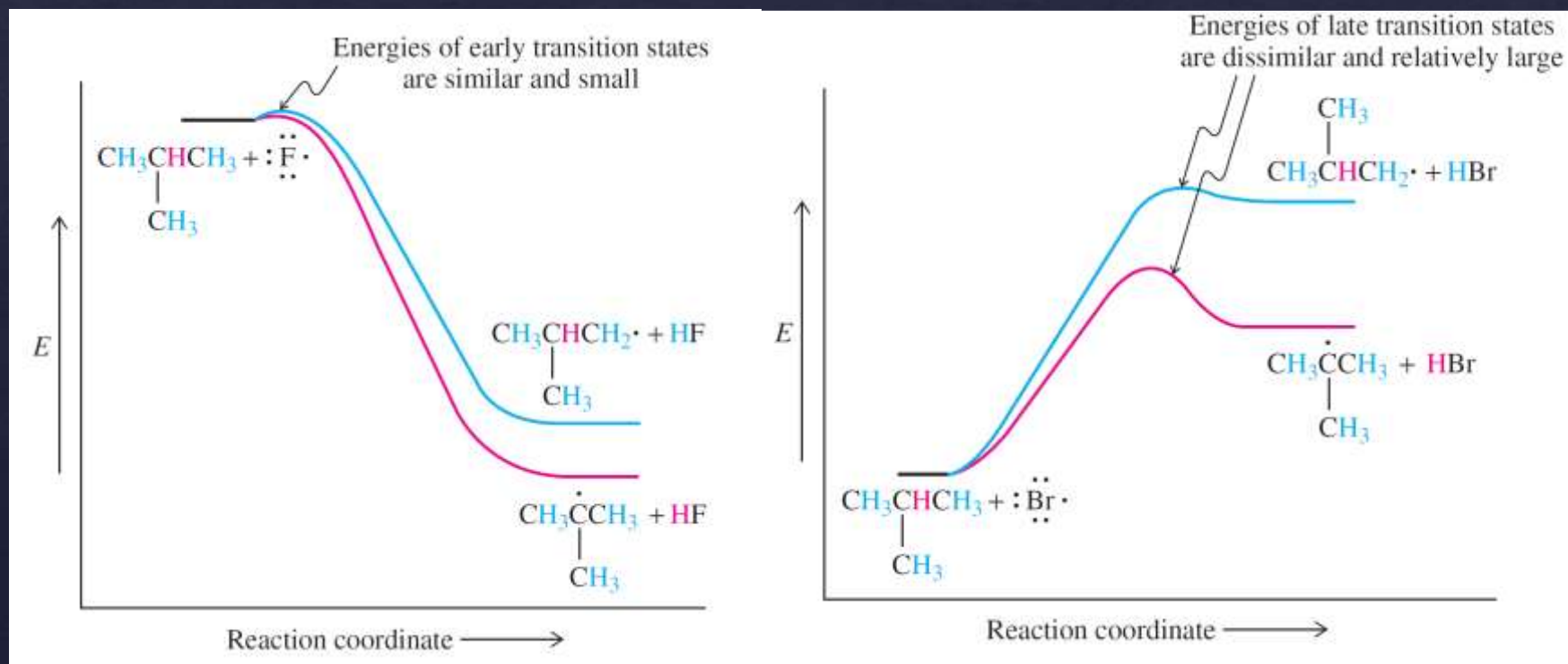
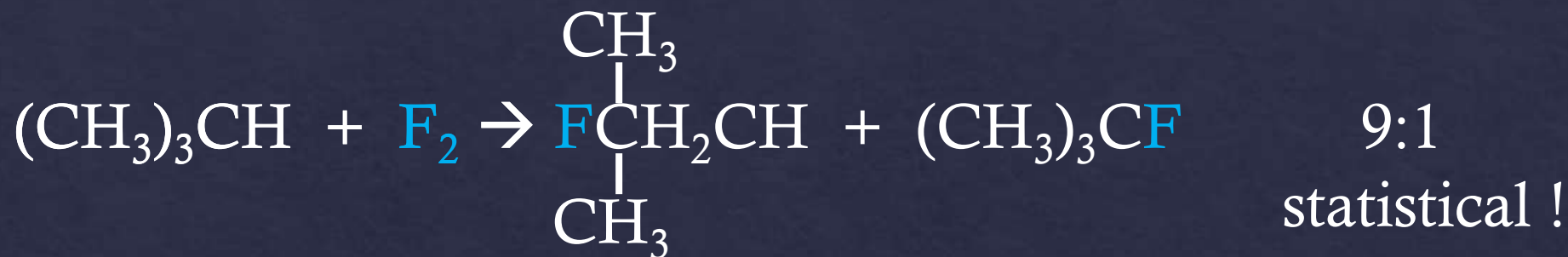


Normalized per H: $64/9 = 7$ $36/1 = 36$
1 5

Result: Relative reactivity (selectivity) in chlorinations at 25 °C: *Tert* : *Sec* : *Prim* = ~ 5 : 4 : 1



Selectivity and other halogens



Just to get a feel for the numbers...

Table 3.6 Relative Reactivities of the Four Types of Alkane C–H Bonds in Halogenations

C–H bond	F· (25°C, gas)	Cl· (25°C, gas)	Br· (150°C, gas)
CH ₃ –H	0.5	0.004	0.002
RCH ₂ –H ^a	1	1	1
R ₂ CH–H	1.2	4	80
R ₃ C–H	1.4	5	1700

^aFor each halogen, reactivities with four types of alkane C–H bonds are normalized to the reactivity of the primary C–H bond.

Primary
Primary, longer C-chain
Secondary
Tertiary

Picture from Vollhardt & Schore

Selectivities vary extensively with the reagent employed, e.g., ICl, ROCl, R₂NBr, with temperature, and solvent.

Why is this important?

Halogenation converts nonfunctional alkanes into functionalized haloalkanes



starting materials for a variety of subsequent transformations

The process has to be: safe, economic, selective, efficient