Organic Chemistry 1
Lecture 7

Instructor: Prof. Duncan Wardrop

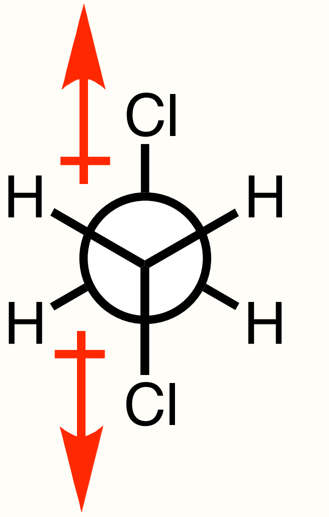
Time/Day: T & R, 12:30-1:45 p.m.

February 02, 2010

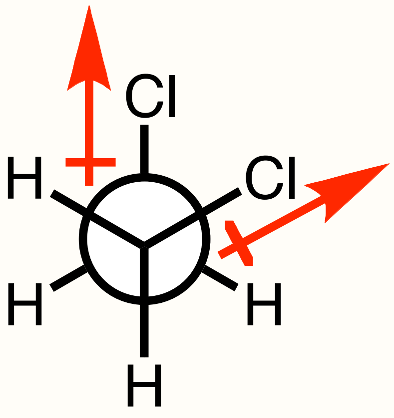
Self Test Question

The measured dipole of $\mathrm{ClCH_2CH_2Cl}$ is 1.12D. Which one of the following statements about 1,2-dichloroethane must be false?

Hint: Draw all non-eclipsed conformations.



antiperiplanar



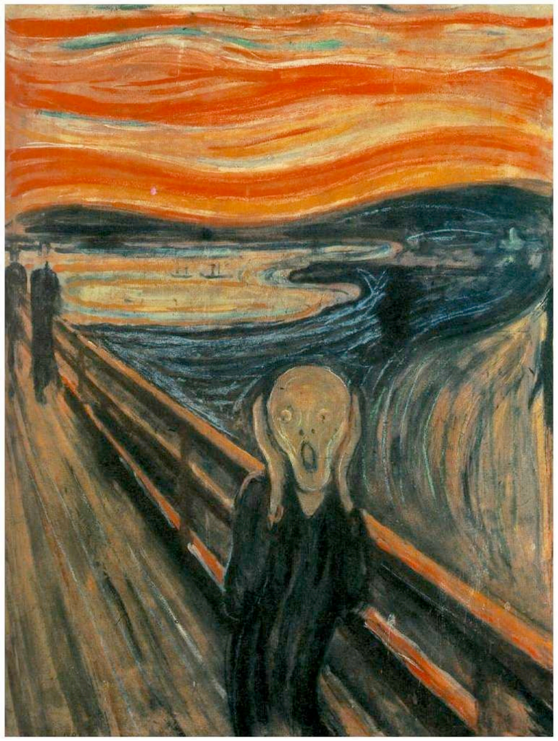
gauche

A. It may exist entirely in the *anti* conformation

B. It may exist entirely in the gauche conformation.

C. It may exist as a mixture of *anti* and *gauche* conformations.

The answer is A. If 1,2-dichloroethane existed only in the antiperiplanar conformation, the individual C–Cl bond dipoles would cancel each other out and the bulk dipole would be much smaller than 1.12 Debye (D). Without a knowledge of the magnitude of the bond dipoles, we cannot discount answers B and C.



Exam One

When: Monday, February 15
Time: 6:00-7:15 p.m.
Where: 250 SES
Material: Chapters 1-5 (everything!)
Makeup Exam: Monday, Feb. 22, time t.b.a.

Makeup policy: There are no makeup exams without **prior** approval. Only students showing proof of a class conflict will have the option to take a makeup exam. To be added to the makeup list, you must email me no later than Friday, Feb. 12.

Exam One Tentative Format (75 min)

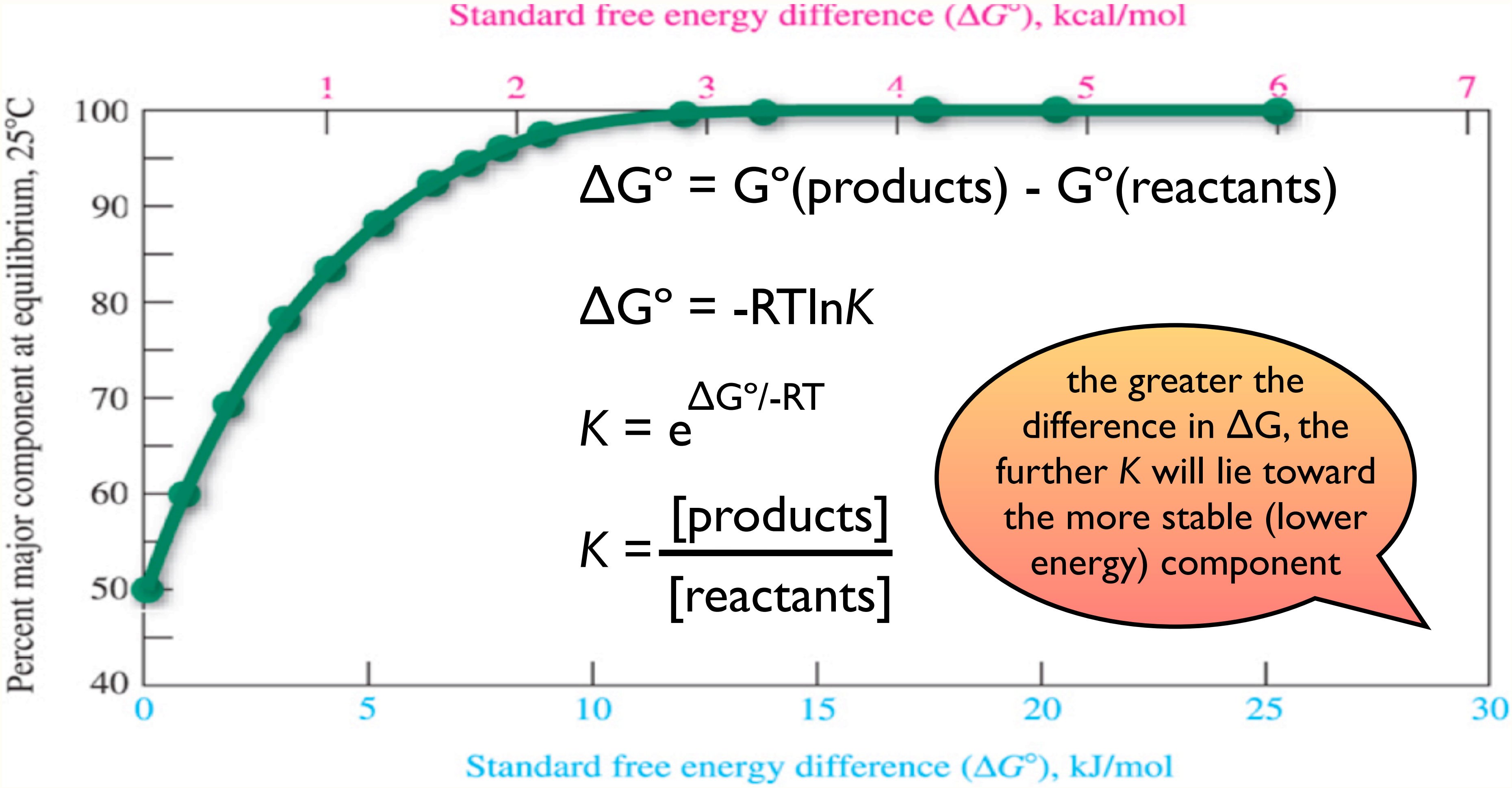
Ranking: 60 points
Naming: 30 points
Drawing: 40 points
Predict the Products: 40 points
Mechanisms: 40 points
Short Answer: 40 points
TOTAL: 250 points

Chapter 3

Clarification of “Issues”

Free Energy, Enthalpy, Equilibrium

$$\text{reactants} \xrightleftharpoons{K} \text{products}$$



$\Delta G° = G°(\text{products}) - G°(\text{reactants})$

$\Delta G° = -RT\ln K$

$K = e^{\Delta G°/-RT}$

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

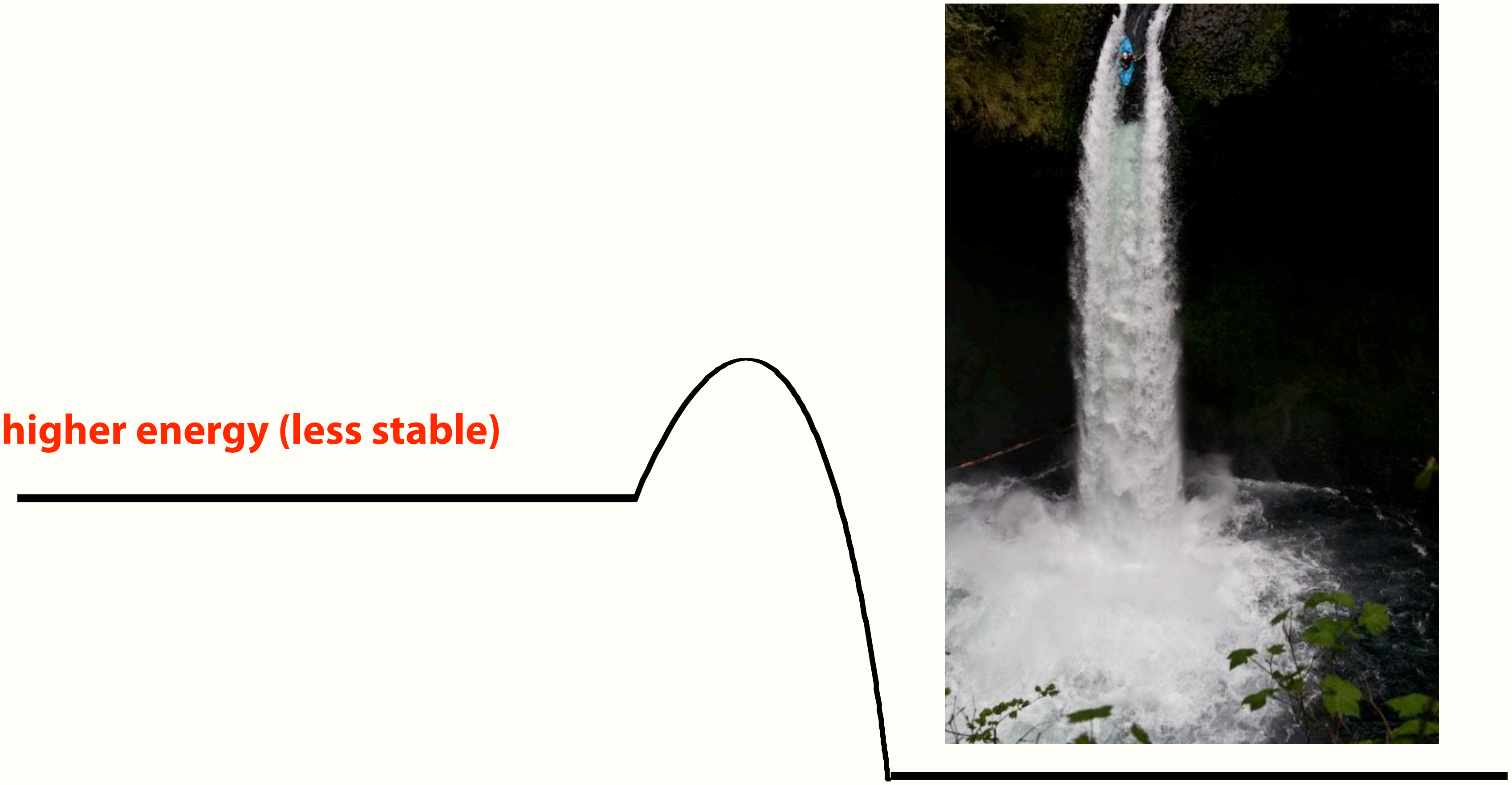
the greater the difference in ΔG, the further *K* will lie toward the more stable (lower energy) component

For a useful discussion of free energy and equilibrium, see:

http://www.chem1.com/acad/webtext/thermeq/TE5.html

Second Law of Thermodynamics

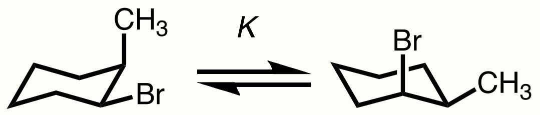
natural systems tend to move toward lower potential energy and higher entropy

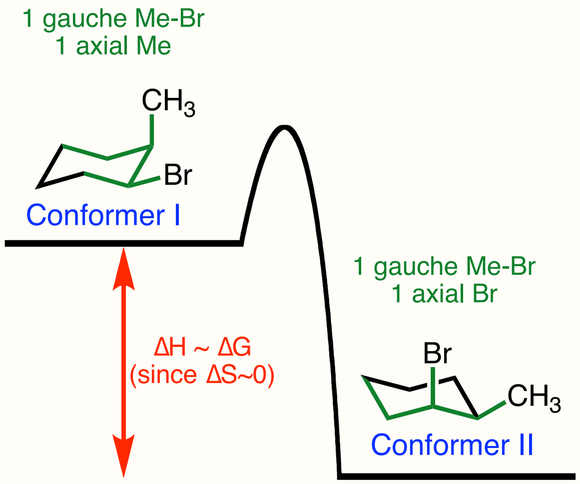


higher energy (less stable)

lower energy (more stable)

Determining ΔG and K_a in Cyclohexanes





Incremental Torsional Strain Energies

Adjacent Groups	Relationship	Strain Energy
H – H	gauche	0
H – CH_3	gauche	0
CH_3-CH_3	gauche	3.8 kJ/mol
CH_3– Br	gauche	3.8 kJ/mol
H – H	eclipsed	4.0 kJ/mol
H – CH_3	eclipsed	5.8 kJ/mol
CH_3 – CH_3	eclipsed	11 kJ/mol

Cyclohexane Axial Strain Energies

Axial Group	Strain Energy
-CH_3	7.3 kJ/mol
–CH_2CH_3	7.5 kJ/mol
–$C(CH_3)_3$	20 kJ/mol
–Br	2.5 kJ/mol
–Cl	2.5 kJ/mol
–OH	2.5 kJ/mol

$$\Delta G^o = G^o(\text{products}) - G^o(\text{reactants})$$

$$\Delta G^o = (3.8 + 2.5) - (3.8 + 7.3)$$

$$\Delta G^o = -4.8 \text{ kJ/mol}$$

$$\Delta G^o = -4800 \text{ J/mol}$$

$$K = \exp(\Delta G^o/-RT)$$

$$K = \exp[(-4800)/(-8.314*298)]$$

$$K = 6.9$$

$$K = [\text{prod}]/[\text{react}]$$

$$K = 6.9/1$$

$$\%\ \text{prod} = 6.9/7.9 = 87\%$$

$$\%\ \text{react} = 1/7.9 = 13\%$$

The strain energy energy of the right-hand-side conformer results from i) 1 axial bromine atom (2.5 kJ) and ii) one gauche butane interaction between the bromine atom and the methyl group. The strain energy of the other conformer, relative to cyclohexane, arises from i) an axial methyl group; ii) 1 gauche butane interaction between the methyl and bromine.

Self Test Question

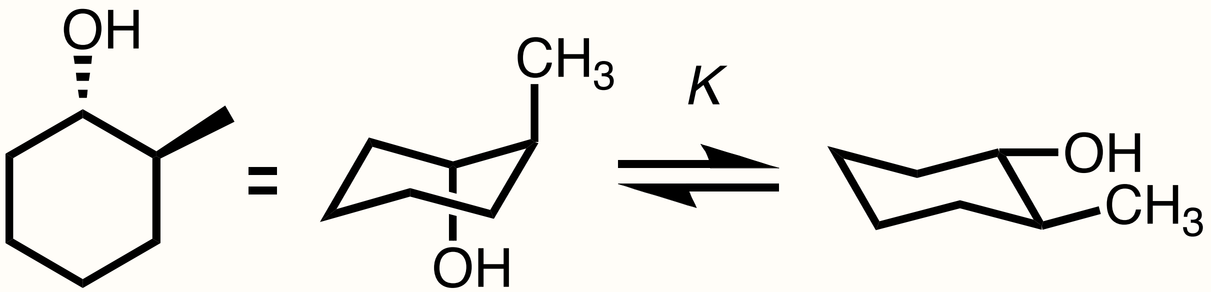
Determine the equilibrium constant (*K*) for the ring-inversion of *trans*-2-methylcyclohexanol shown below?

Incremental Torsional Strain Energies

Adjacent Groups	Relationship	Strain Energy
CH_3-$CH_{3/2}$	gauche	3.8 kJ/mol
OH – $CH_{3/2}$	gauche	3.8 kJ/mol
H – H	eclipsed	4.0 kJ/mol
H – CH_3	eclipsed	5.8 kJ/mol
CH_3 – CH_3	eclipsed	11 kJ/mol

Cyclohexane Axial Strain Energies

Axial Group	Strain energy
-CH_3	7.3 kJ/mol
–Br	2.5 kJ/mol
–OH	2.5 kJ/mol



$\Delta G^o = G^o(\text{prod}) - G^o(\text{react})$

$\Delta G^o = (3.8) - (2.5+7.3)$

$\Delta G^o = -6.0$ kJ/mol

$K = \exp(\Delta G^o/-RT)$

$K = \exp[(-6000)/-(8.314*298)]$

$K = 11$

A. 6.0

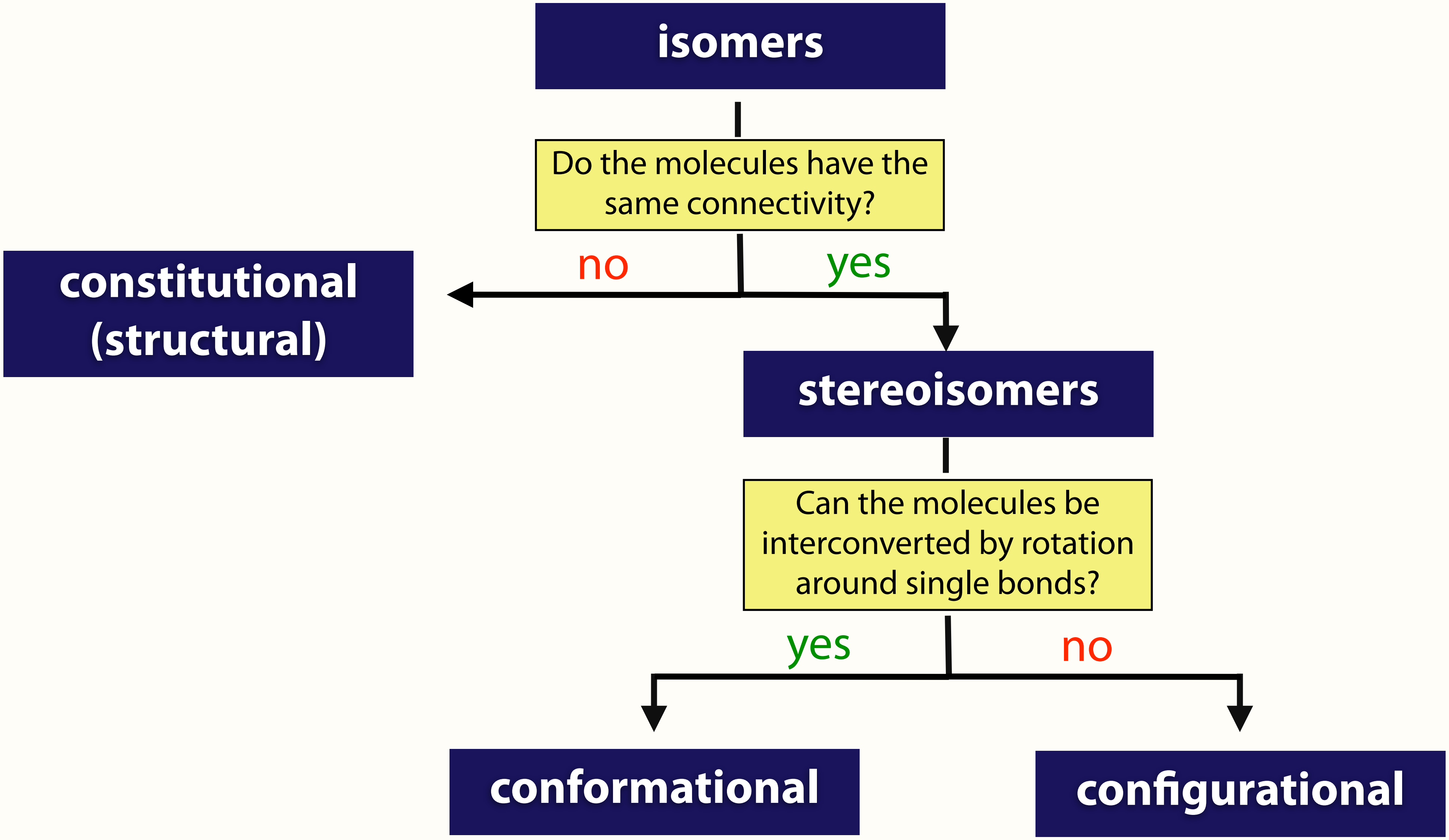
B. 11

C. 52

D. 9.8

E. 0.09

Constitutional vs. Configurational Isomers



isomers

Do the molecules have the same connectivity?

no

yes

constitutional (structural)

stereoisomers

Can the molecules be interconverted by rotation around single bonds?

yes

no

conformational

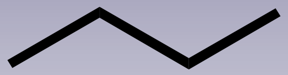
configurational

Comparison

Constitutional (Structural) Isomers

- same molecular formula
- atoms bonded in different order
- a.k.a.: different connectivity

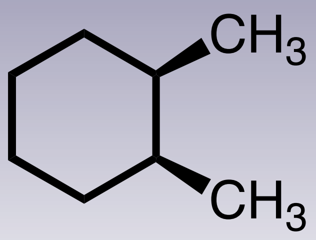
isobutane



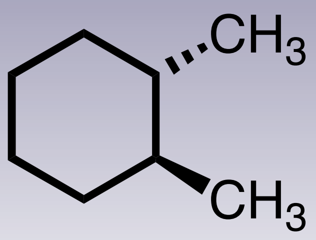
butane

Configurational Stereoisomers

- same molecular formula
- same connectivity
- different arrangement of atoms in space that cannot be interconverted by bond rotation



cis-1,2-dimethyl cyclohexane



trans-1,2-dimethyl cyclohexane

Chapter 4

Alcohols and Alkyl Halides

Functional Groups

Alcohols and Alkyl Halides

Section: 4.1

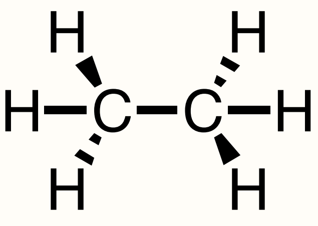
Functional Groups

<u>functional group</u>: a defined connectivity for a specific group of atoms (≥2) within a molecule

since alkanes are chemically inert, functional groups are responsible for chemical reactivity under specific conditions and also the physical, chemical and biological properties of organic molecules

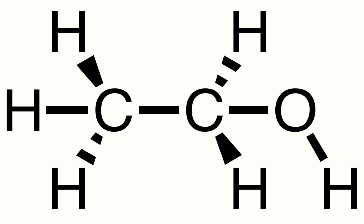
b.p. -88.6 °C

Inert to acids, bases, oxidizing & reducing agents



Ethane

vs.



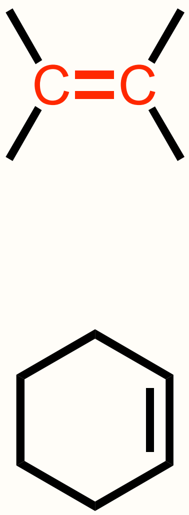
Ethanol

b.p. = 78.4 °C

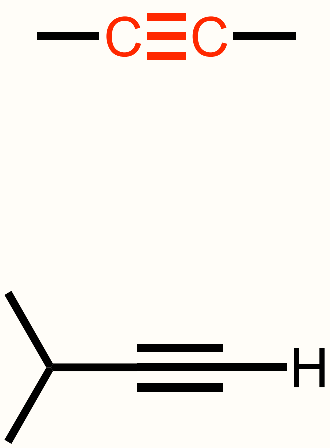
Reacts with acids, bases, oxidizing & reducing agents Biologically Active!

Examples of Functional Groups

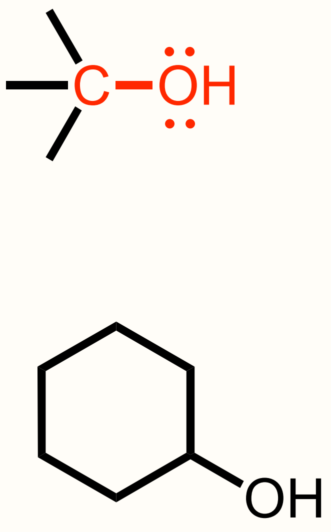
alkene



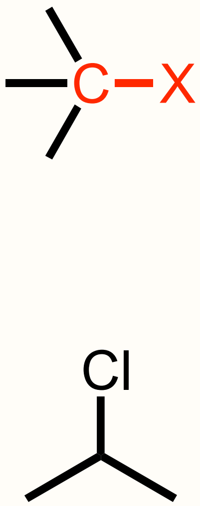
alkyne



alcohol

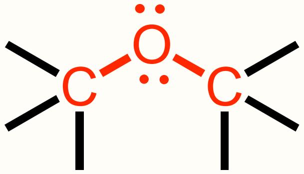


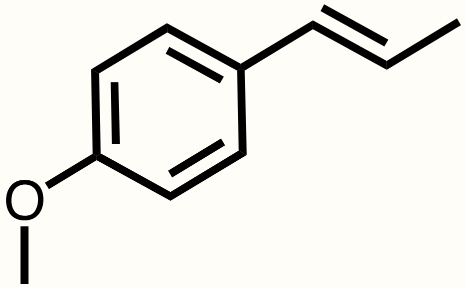
alkyl halide



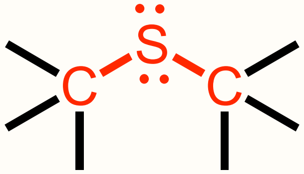
Examples of Functional Groups

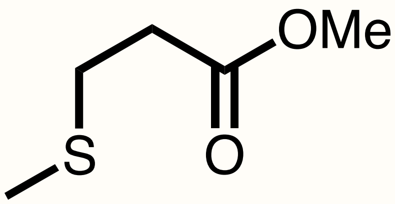
ether

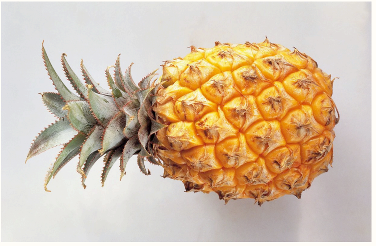




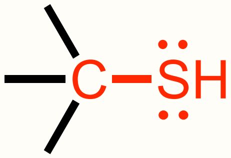
sulfide

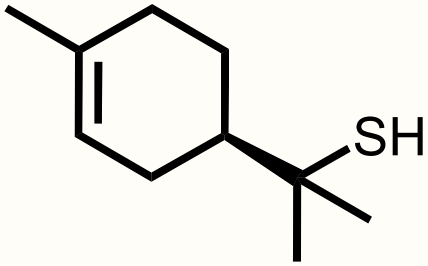




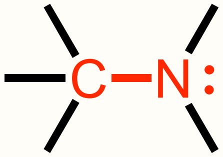


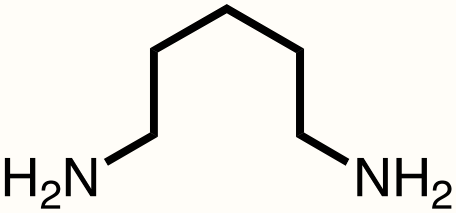
thiol





amine

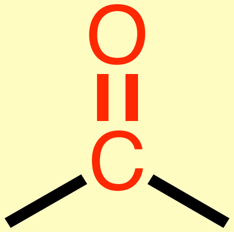




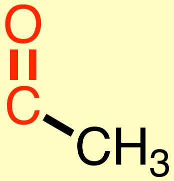
The molecules shown above are anethole (an ether found in toothpaste and Ouzo); methyl 3-(methylthio)propanoate (a sulfide responsible for the smell and taste of pineapples); (R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol (a thiol partly responsible for the odor of fresh squeezed grapefruit juice); putrescine (an amine or, more correctly, a diamine responsible for a number of fouls odors, including putrefying flesh and bad breath).

Carbonyl Functional Groups: Carboxylic Acid Derivative

carbonyl group



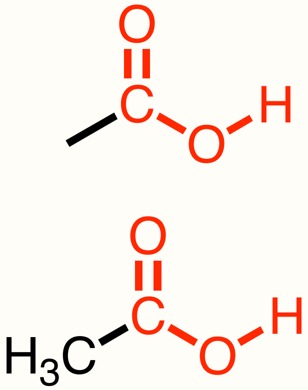
pervasive common name



acetyl

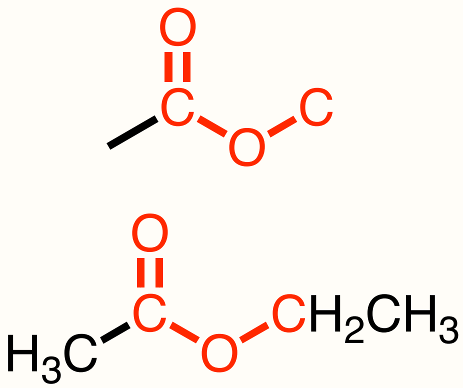
acet-

carboxylic acid



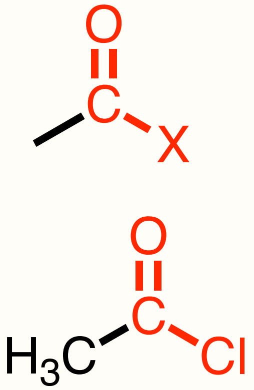
acetic acid

ester



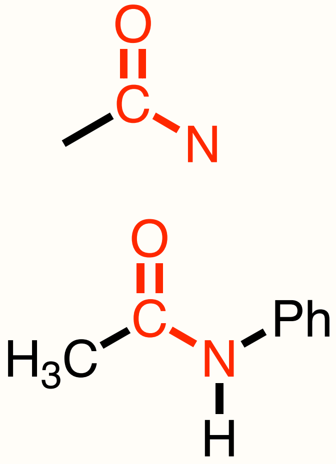
ethyl acetate

acid halide



acetyl chloride

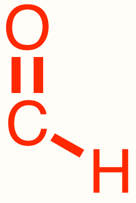
amide

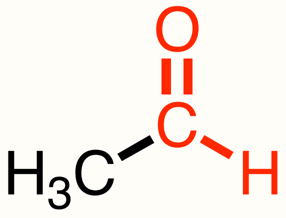


acetanilide

Carbonyl Functional Groups

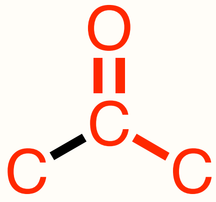
aldehyde

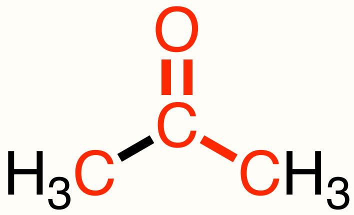




acetaldehyde

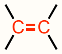
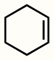
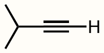
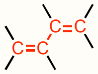
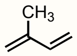
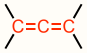
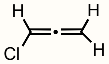
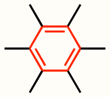
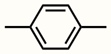
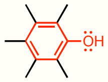
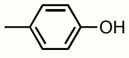
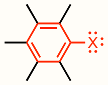
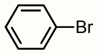
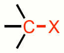
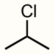
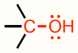
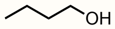
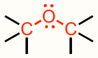
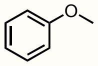
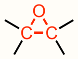
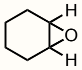
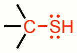
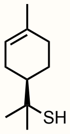
ketone





acetone

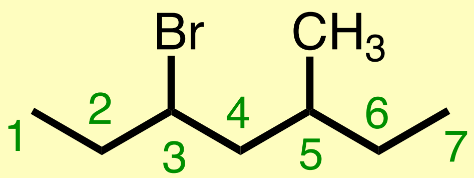
Time to Memorize Functional Groups!

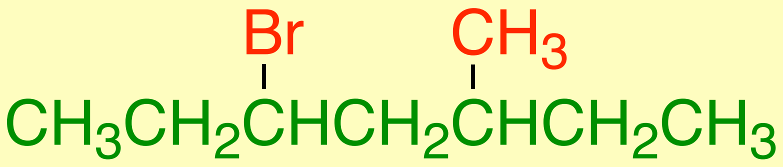
Functional Group (F.G.)	F. G. Class	Example	IUPAC Name	"Trivial" Name
	Alkene		cyclohexene	cyclohexene
	Alkyne		3-methylbut-1-yne	isopropyl acetylene
	1,3-Diene		2-methylbuta-1,3-diene	isoprene
	Allene		1-chloropropa-1,2-diene	chloroallene
	Arene		1,4-dimethylbenzene	*p*-xylene
	Phenol		4-methylphenol	*p*-cresol
	Aryl halide		bromobenzene	bromobenzene
	Alkyl halide		2-chloropropane	isopropyl chloride
	Alcohol		butan-1-ol	*n*-butanol
	Ether		methoxybenzene	anisole
	Epoxide		7-oxabicyclo[4.1.0]heptane	cyclohexene oxide
	Thiol		(*R*)-2-(4-methylcyclohex-3-enyl)propane-2-thiol	grapefruit thiol

- many already encountered - alkenes, alkynes, arenes <u>not alkanes</u>
- study functional group handout from website - learn to draw & name F.G.s
- make flash cards
- you will be asked to identify and name functional groups on quiz 3 & first exam

http://www.chem.uic.edu/chem232/page7

IUPAC (Substitutive): Alkyl Halides





$$CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_3$$

3-bromo-5-methylheptane

Steps:

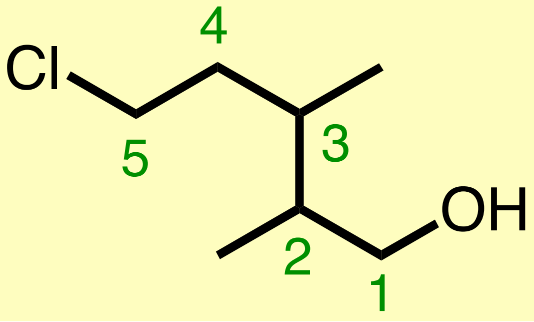
1. Identify and number the longest continuous chain of carbons.
2. Follow all previous rules and conventions for naming/numbering alkane chains.
3. Name the compound according to the figure below.

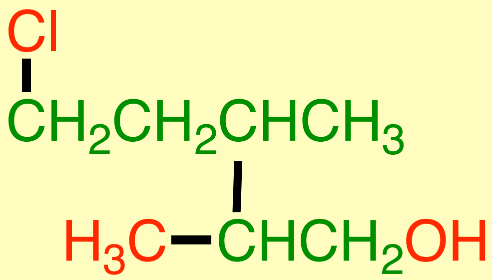
Conventions:

- Previous conventions apply (e.g., first point of difference rule).
- Halogens and alkyl groups are considered to have *equal rank* when deciding numbering. If two numbering schemes give same locant, choose numbering that lists substituents alphabetically.
- Subsituent names for halogens are *fluoro*, *chloro*, *bromo*, & *iodo*.

parent locant — **halo substituent** **parent chain name**

IUPAC (Substitutive): Alcohols





$$\begin{array}{l} \text{Cl} \\ | \\ \text{CH}_2\text{CH}_2\text{CHCH}_3 \\ \qquad\qquad\quad | \\ \qquad \text{H}_3\text{C}-\text{CHCH}_2\text{OH} \end{array}$$

5-chloro-2,3-dimethyl-pentan-1-ol *or* 5-chloro-2,3-dimethyl-1-pentanol

Steps:

1. Identify and number the longest continuous chain of carbons to give the -OH group the lowest locant.
2. Name the parent by replacing *-e* with *-ol* (e.g. pentane becomes pentanol).
3. Name the compound according to the figure below.

Conventions:

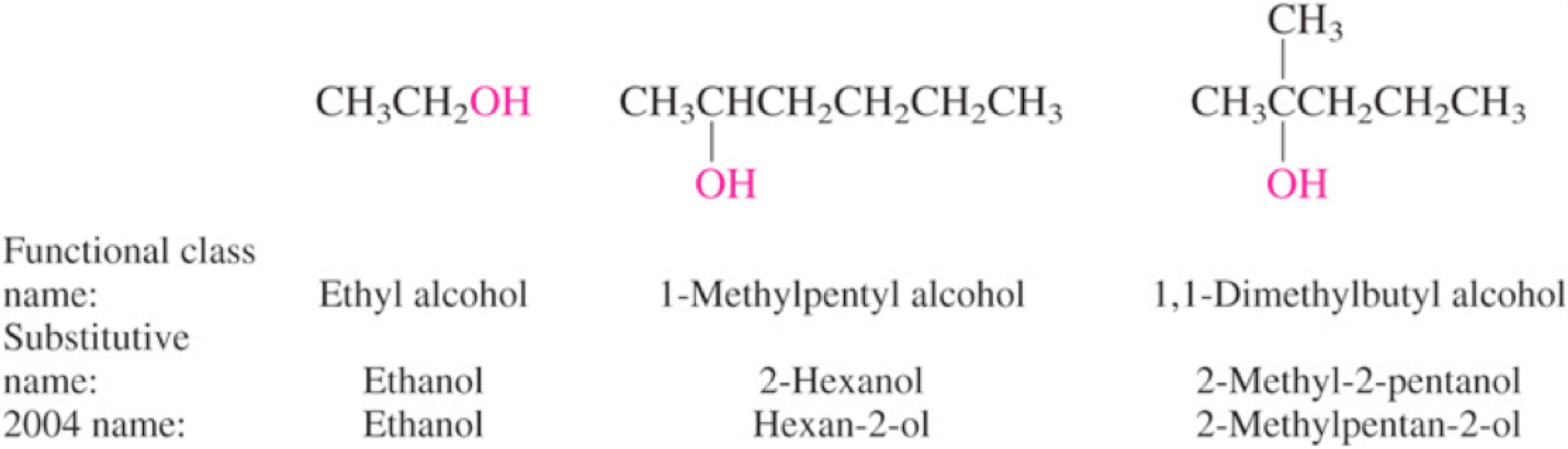
- Previous conventions apply (e.g., first point of difference rule).
- Alcohols *outrank* (have priority over) halogens and alkyl groups when considering numbering scheme.
- Alcohol locant may be placed before the parent name (e.g. 1-pentanol) or after (e.g. pent-1-ol).

locant — **parent (drop last "e")** **"ol"**

parent (drop last "e") — **locant** — **"ol"**

Note that the name is ...pentan-1-ol and not ...pent-1-ol, as originally noted.

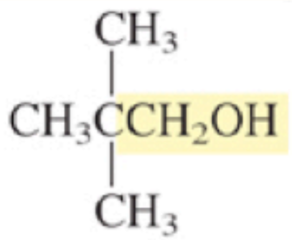
Two Substitutive Nomenclatures vs. Functional Group Class Nomenclature



	CH_3CH_2OH	$CH_3\underset{OH}{C}HCH_2CH_2CH_2CH_3$	$CH_3\overset{CH_3}{\underset{OH}{C}}CH_2CH_2CH_3$
Functional class name:	Ethyl alcohol	1-Methylpentyl alcohol	1,1-Dimethylbutyl alcohol
Substitutive name:	Ethanol	2-Hexanol	2-Methyl-2-pentanol
2004 name:	Ethanol	Hexan-2-ol	2-Methylpentan-2-ol

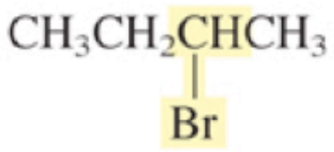
- substitutive and 2004 name are preferred
- exams, quizzes, will only contain substitutive and 2004 names
- old habits are hard to break

Classification of Substituted Carbons



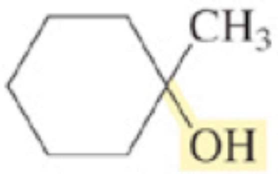
$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2OH$

2,2-Dimethyl-1-propanol
(a primary alcohol)

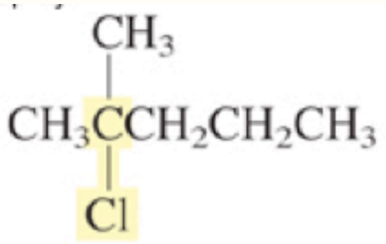


$CH_3CH_2\underset{Br}{CH}CH_3$

2-Bromobutane
(a secondary alkyl halide)



1-Methylcyclohexanol
(a tertiary alcohol)



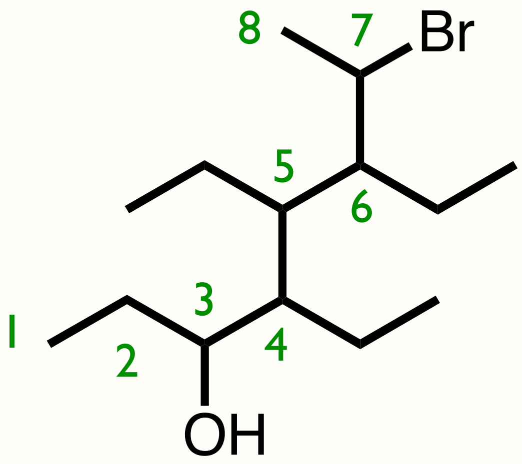
$CH_3\overset{CH_3}{\underset{Cl}{C}}CH_2CH_2CH_3$

2-Chloro-2-methylpentane
(a tertiary alkyl halide)

- count the number of carbons bonded to the carbon atom you wish to classify:
  - one = primary (1°)
  - two = secondary (2°)
  - three = tertiary (3°)
  - four = quaternary (4°)

Self Test Question

What is the IUPAC (substitutive) name for the following molecule?



A. 3-hydroxy-4,5,6-triethyl-7-bromooctane

B. 2-bromo-3,4,5-triethyloctan-3-ol

C. 7-bromo-4,5,6-triethyloctan-3-ol

D. 4-(3-bromo-1,2-diethylbutyl)-3-hexanol

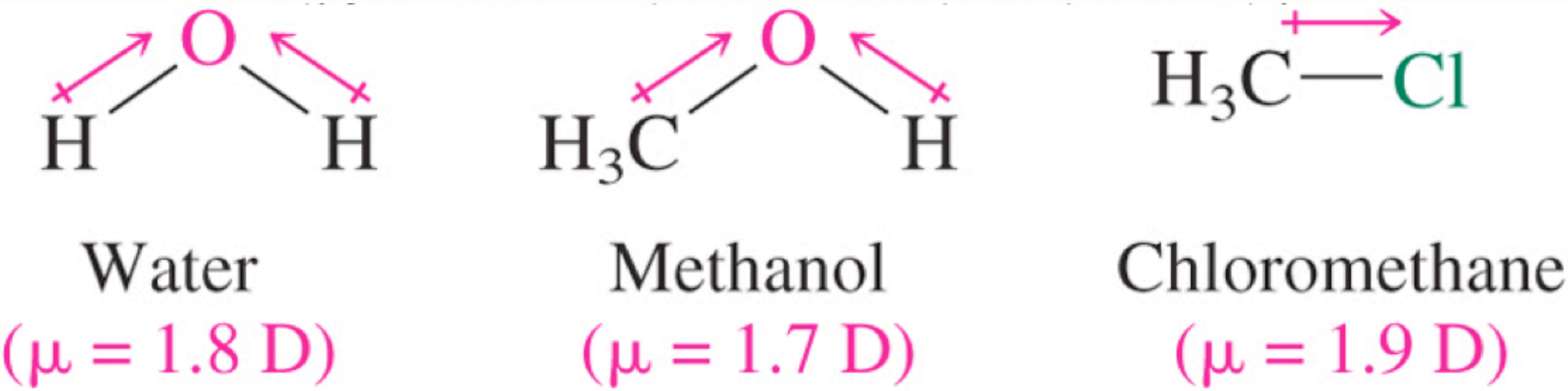
E. 6-(1-bromoethyl)-4,5-diethyl-3-octanol

The answer is C.

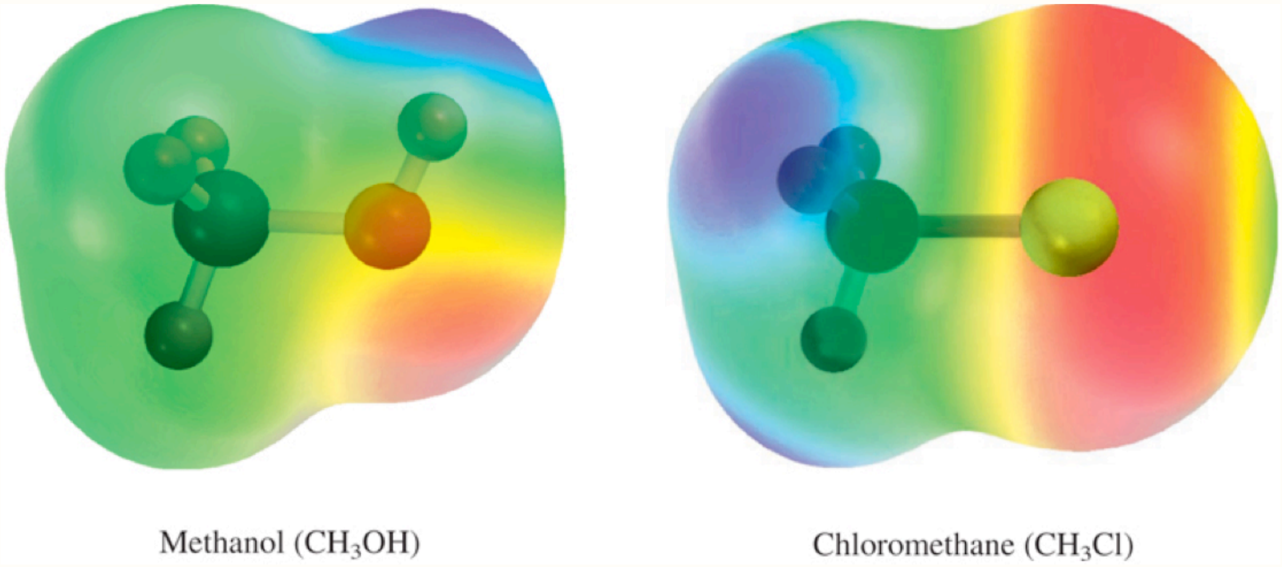
Properties of Alcohols and Alkyl Halides

Sections: 4.5-4.6

Alcohols and Alkyl Halides Are Polar



($\mu = 1.8$ D) ($\mu = 1.7$ D) ($\mu = 1.9$ D)



Methanol (CH_3OH) Chloromethane (CH_3Cl)

red = higher electron density (partial negative charge)

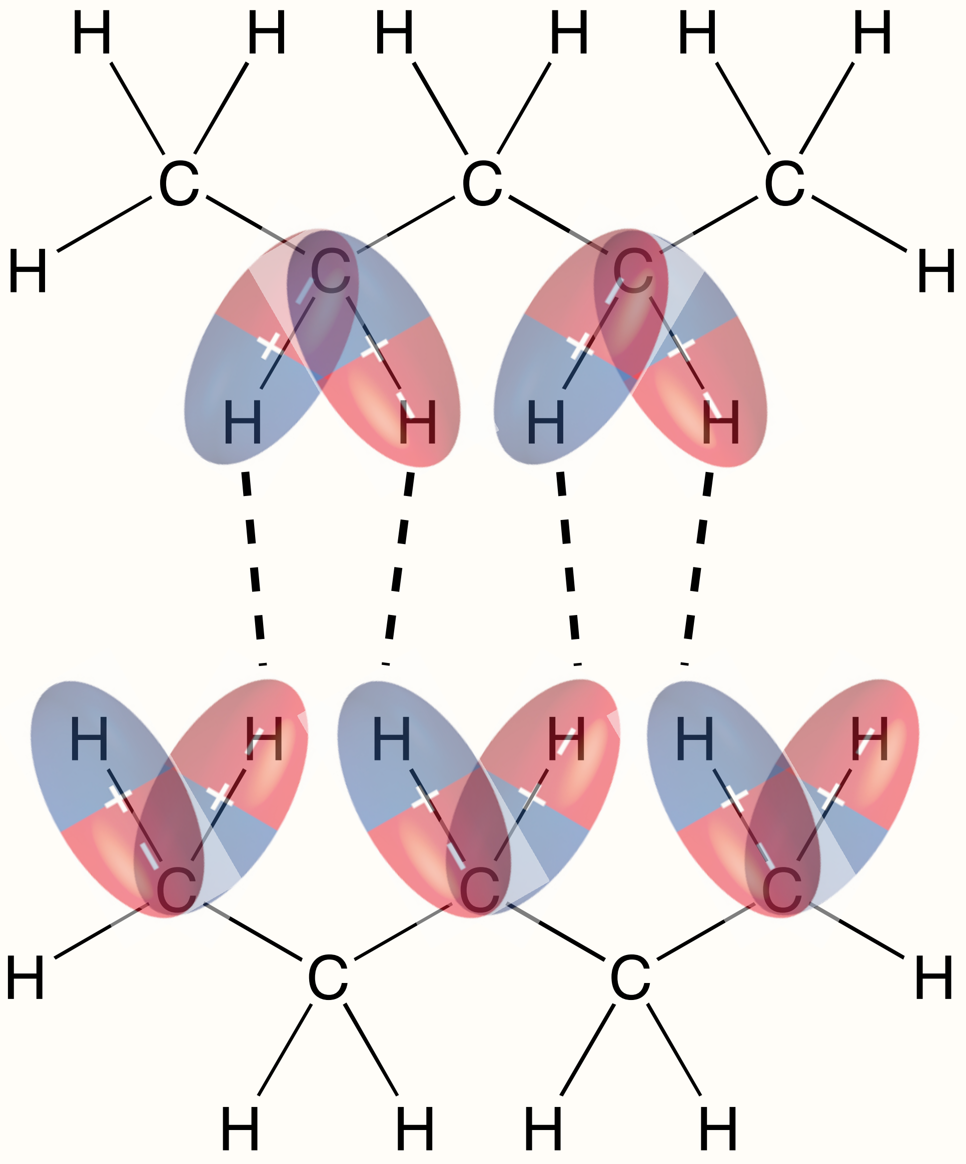
blue = lower/ deficient electron density (partial positive charge)

Notice that not all polar organic solvents are made alike: methanol can form hydrogen bonds with water dissolves in this solvent, while dichloromethane does not. This is why solvents are generally divided into

Effect of Structure on Boiling Points

	• only London dispersion forces • aka: induced-dipole/induced-dipole	• induced/induced • dipole-dipole attractive force • dipole/induced-dipole	• induced/induced • dipole-dipole attractive force • dipole/induced-dipole • hydrogen bonding
	$CH_3CH_2CH_3$ (propane)	CH_3CH_2F (fluoroethane)	CH_3CH_2OH (ethanol)
MW	44	48	46
boiling point (°C)	-42	-32	+78
Dipole moment (μ)	0	1.9	1.7

Review: induced-dipole//induced-dipole (London Dispersion Forces)



more atoms =

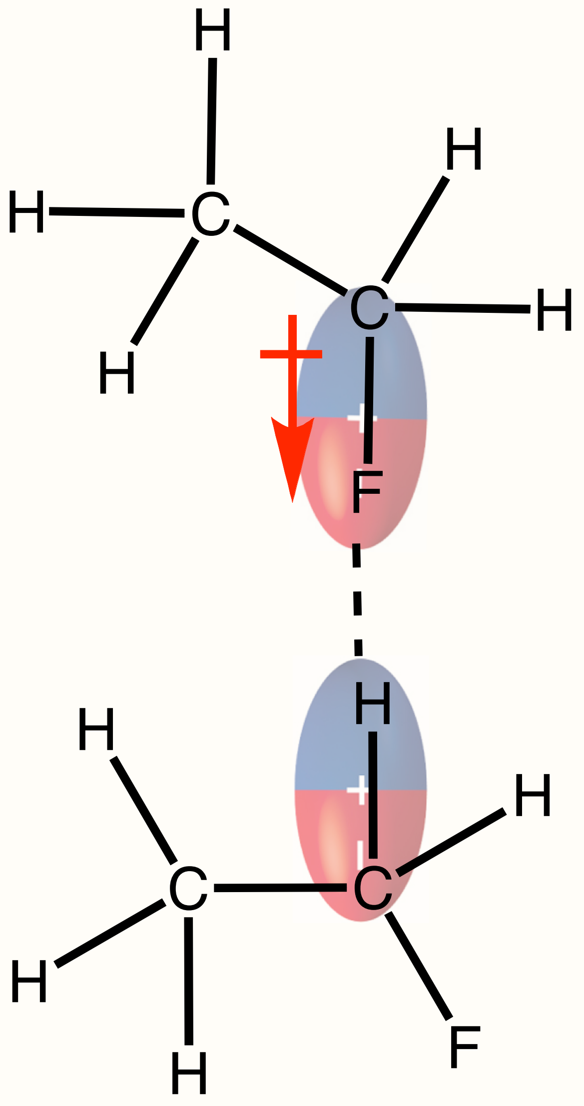
more electrons =

more induced dipoles =

more attractive forces =

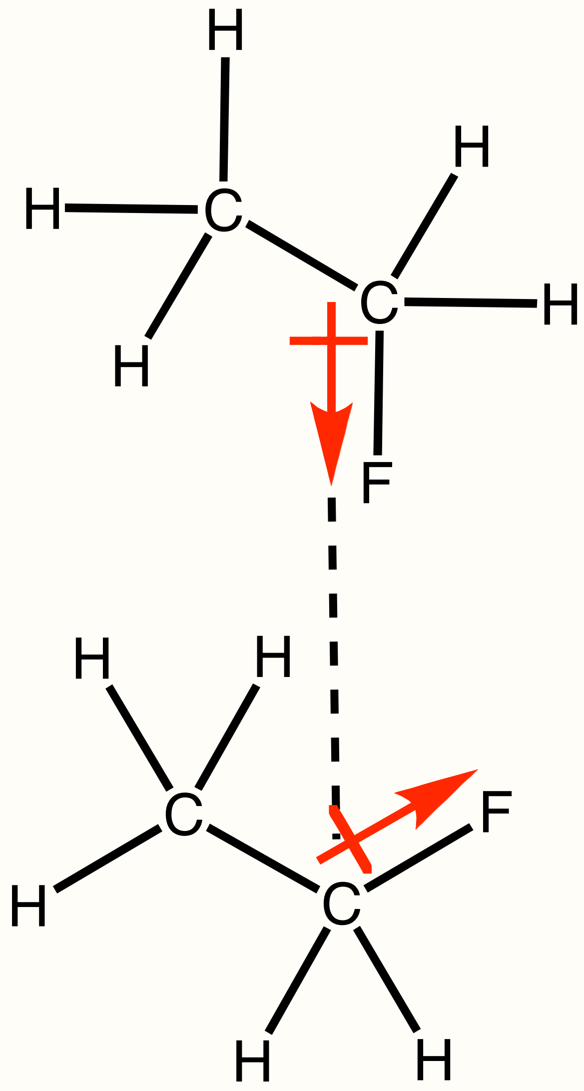
higher boiling point

Dipole/Induced-Dipole



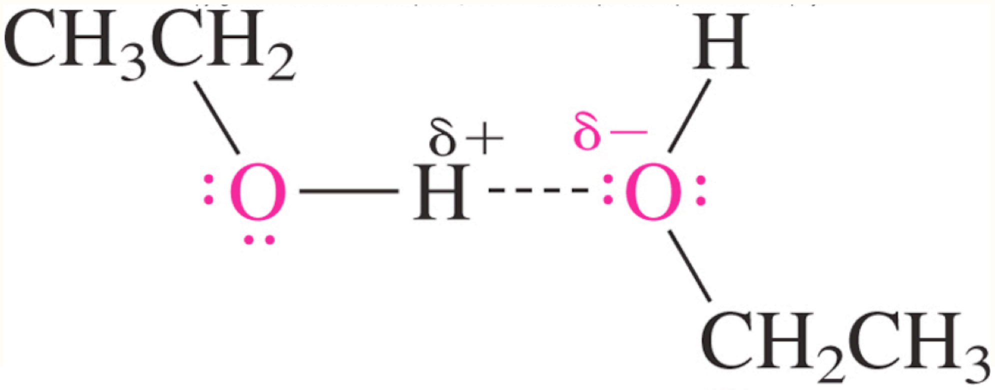
- permanent dipole in one molecule induces a temporary dipole in a non-polar region of another molecule
- more C-X bonds = more dipole/dipole-induced attractive forces

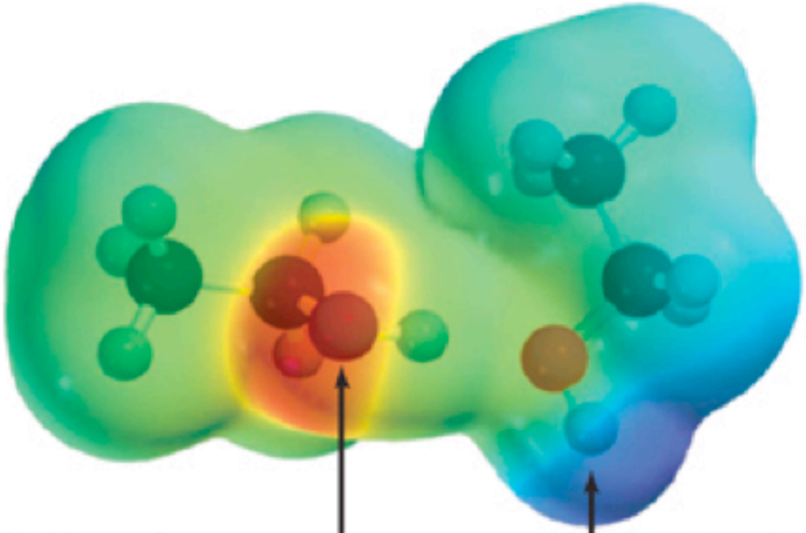
Dipole/Dipole



- attractive force between two permanent dipoles
- not necessarily only at the polar covalent bond: region of partial positive charge in one molecule attracted to region of negative charge in another molecule.

Hydrogen Bonding is a Strong Dipole/Dipole Attractive Force





This oxygen is available to form a hydrogen bond with the OH proton of a third ethanol molecule.

This OH proton is available to form a hydrogen bond with the oxygen of a fourth ethanol molecule.

Boiling Point Trends

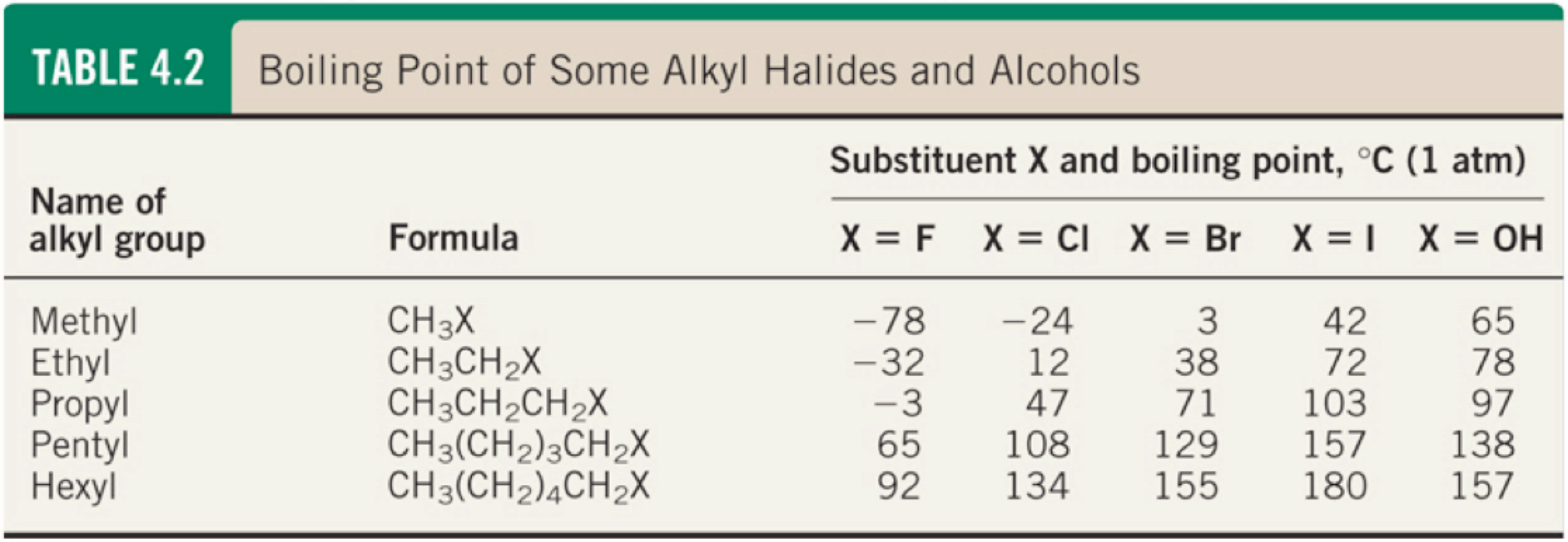


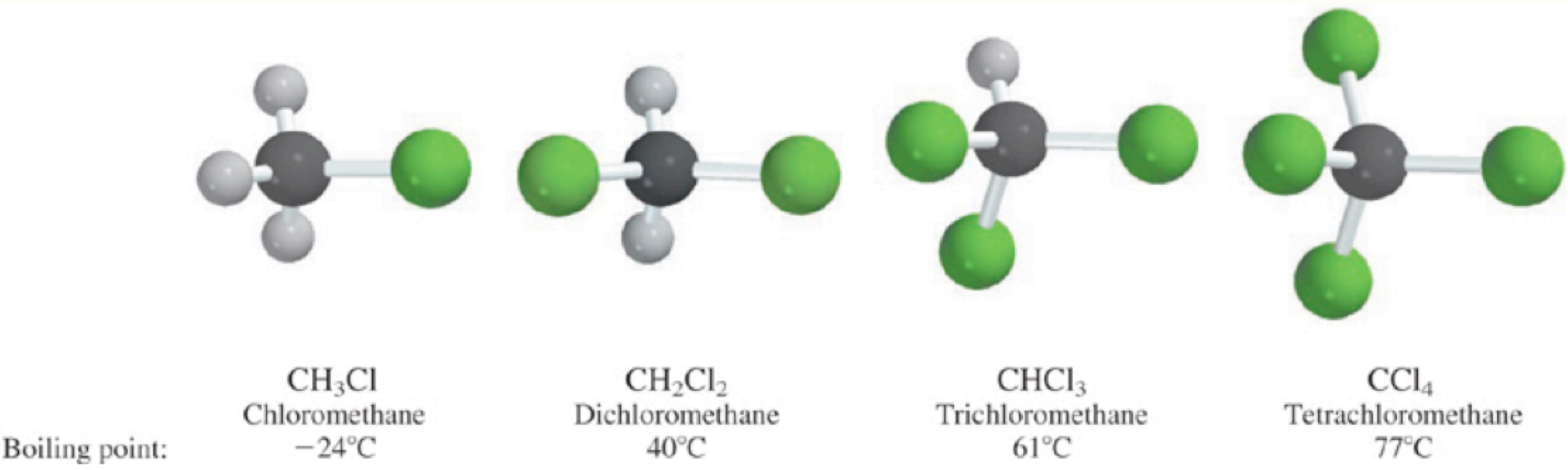
TABLE 4.2 Boiling Point of Some Alkyl Halides and Alcohols

Name of alkyl group	Formula	Substituent X and boiling point, °C (1 atm)				
		X = F	X = Cl	X = Br	X = I	X = OH
Methyl	CH_3X	−78	−24	3	42	65
Ethyl	CH_3CH_2X	−32	12	38	72	78
Propyl	$CH_3CH_2CH_2X$	−3	47	71	103	97
Pentyl	$CH_3(CH_2)_3CH_2X$	65	108	129	157	138
Hexyl	$CH_3(CH_2)_4CH_2X$	92	134	155	180	157

- in same class (i.e. X = F) boiling point increases as MW increases; more atoms = more attractive van der Waals forces = higher boiling point
- alcohols have significantly higher boiling points than similar halides; strong hydrogen bonding attractive forces
- boiling point increases from fluorine to iodine for same series; polarizability of halogen increases down periodic table

Boiling Point Trends (Cl, Br, I Only)

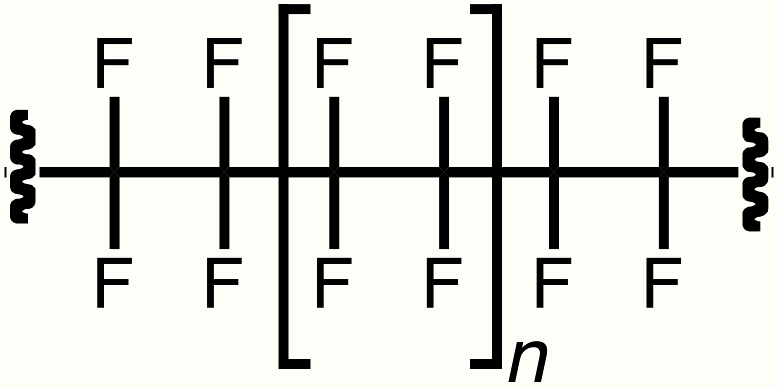
boiling point increases with increasing number of halogens



- despite CCl_4 having no molecular dipole, it has the highest boiling point
- induced-dipole/induced-dipole forces are the greatest because it has the greatest number of chlorine atoms

Polarizability and Teflon

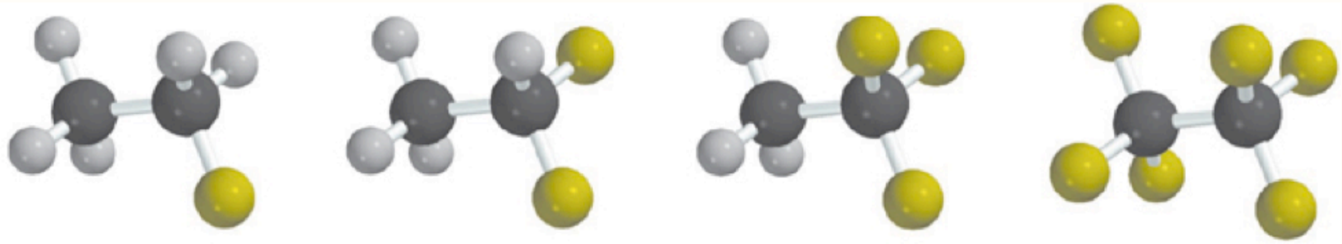
Teflon® = polytetrafluoroethylene (PTFE)



more bonds to F

(low polarizability) =

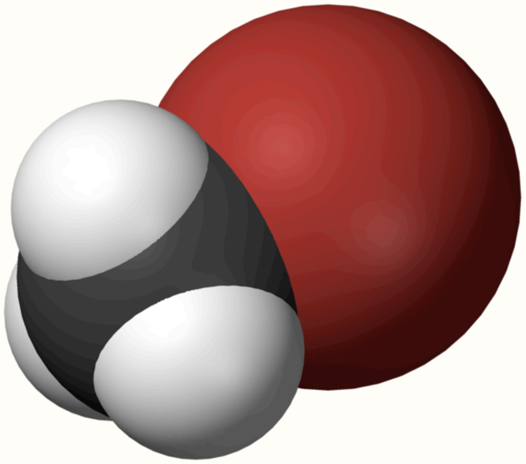
less/weaker induced-dipole/induced-dipole attractive forces



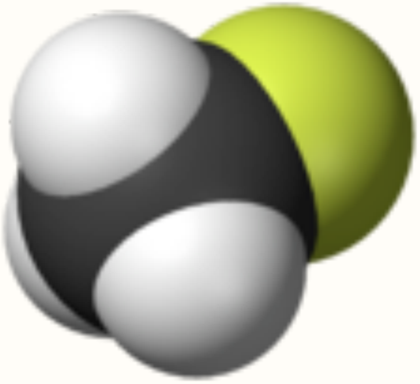
Boiling point:	CH_3CH_2F Fluoroethane −32°C	CH_3CHF_2 1,1-Difluoroethane −25°C	CH_3CF_3 1,1,1-Trifluoroethane −47°C	CF_3CF_3 Hexafluoroethane −78°C

Polarizability

polarizability: the ease of distortion of the electron cloud of a molecular entity by an electric field; “flexibility”, “squishiness” of the electron cloud



bromomethane
(b.p. = 3 ^{o}C)



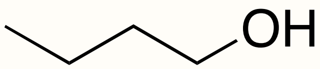
fluoromethane
(b.p. = -78 ^{o}C)

- polarizability increases down the periodic table; larger orbitals; more polarizable =
- better able to momentarily generate induced-dipole =
- stronger induced-dipole/ induced-dipole forces =
- more attractive forces =
- higher boiling point

Self Test Question

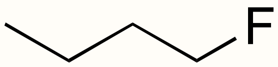
Rank the following in order of *increasing* boiling point.

a.

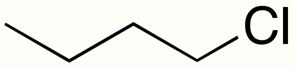


highest

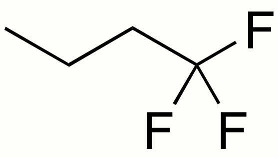
b.



c.



d.



lowest

A. a, b, c, d

B. b, c, d, a

C. b, d, c, a

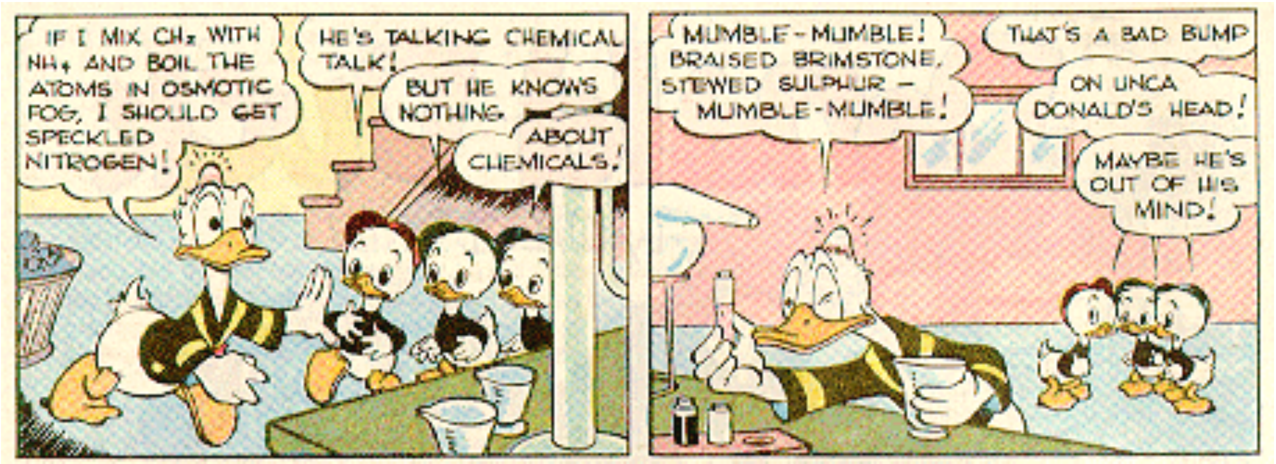
D. a, c, b, d

E. d, b, c, a

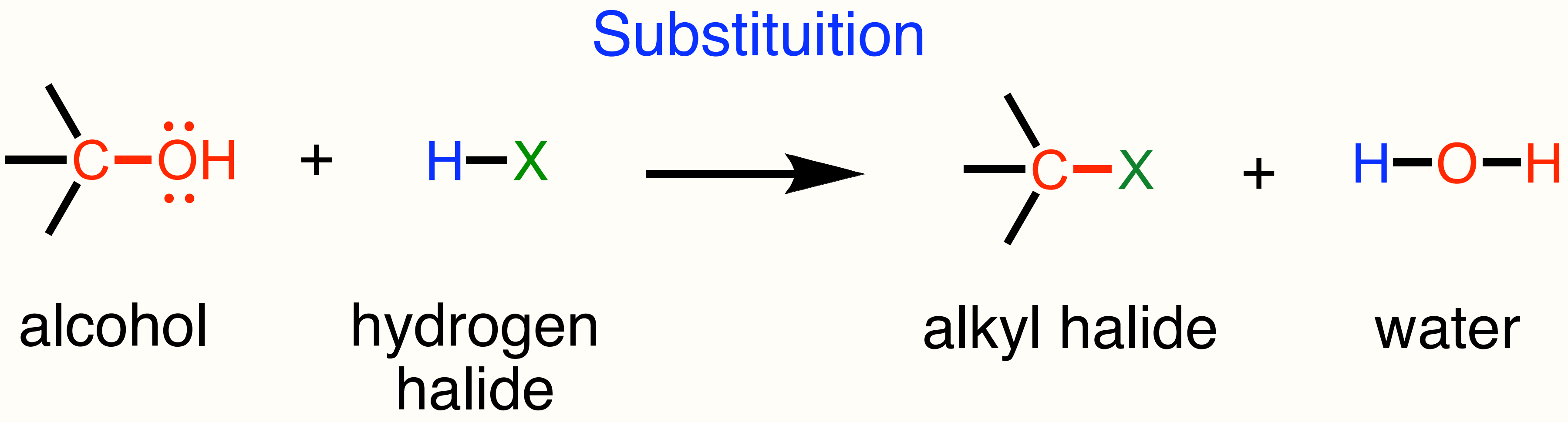
Organic Reactions

Preparation of Alkyl Halides

Sections: 4.7-4.9, 4.13



Preparation of Alkyl Halides from Alcohols



- 1°, 2° & 3° alcohols react
- irreversible reaction; no equilibrium here
- more reactive reactants & substrates = faster reaction

Reactivity of Hydrogen Halides

Increasing Reactivity of Hydrogen Halides Toward Alcohols

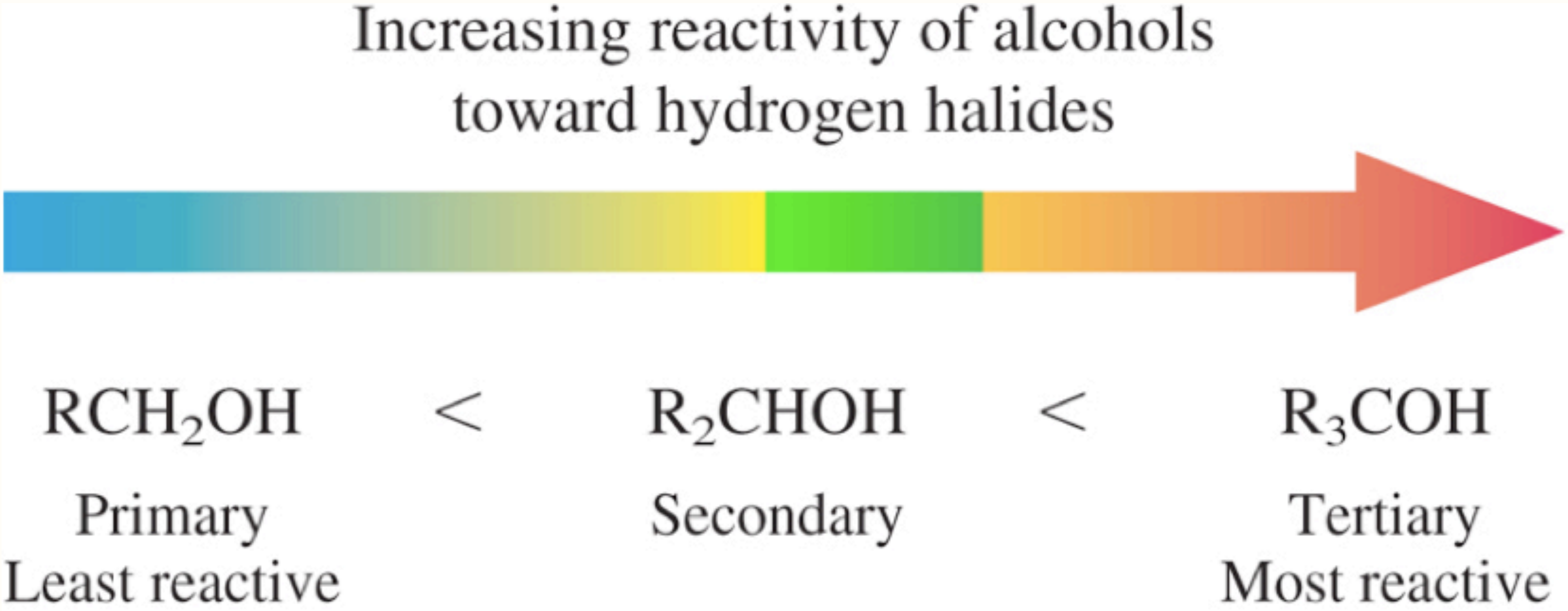
HF < HCl < HBr < HI

least reactive (slowest)

most reactive (fastest)

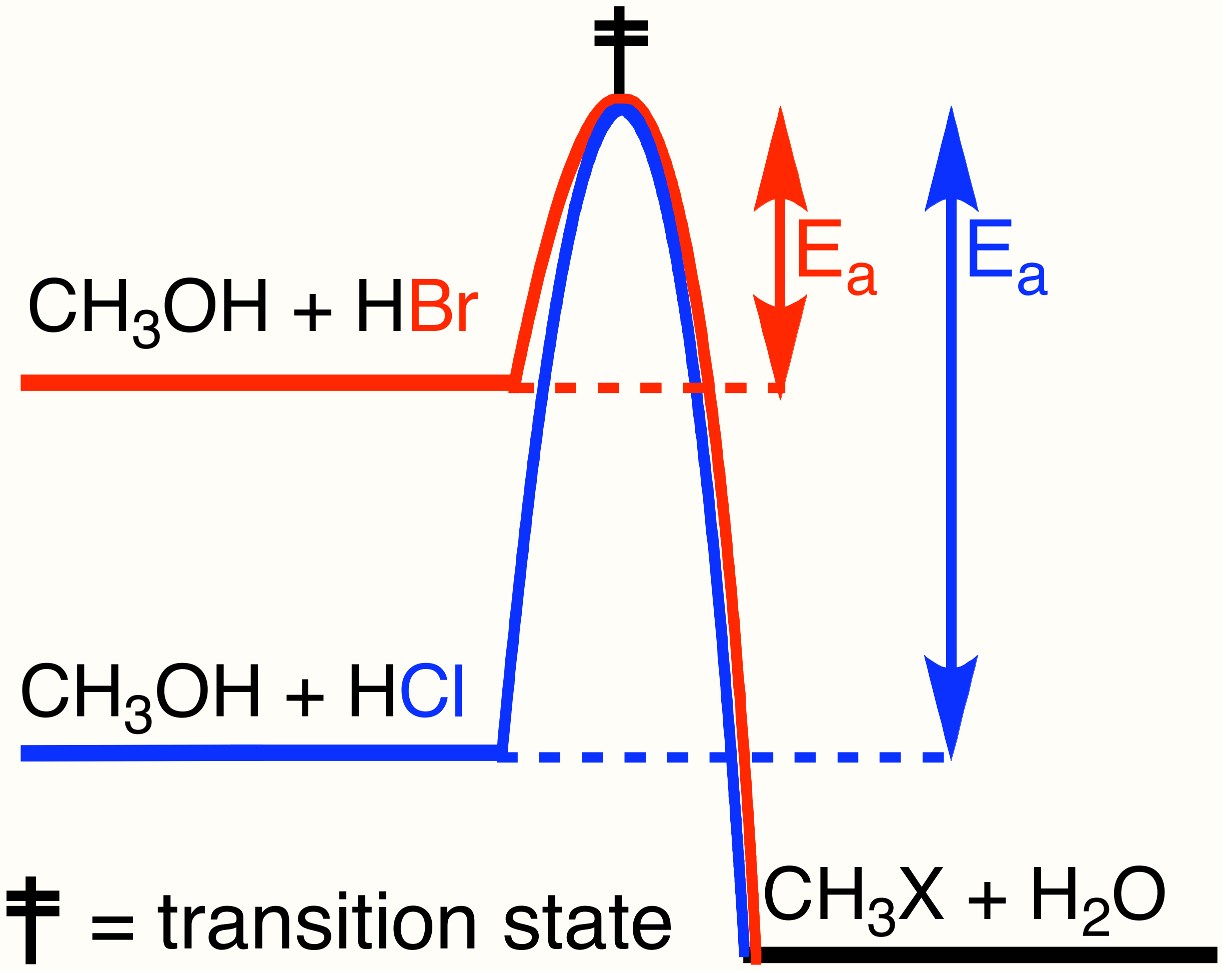
- stronger acid (lower pKa) = more reactive
- increased reactivity = faster reaction
- remember: irreversible reaction; no equilibrium here

Reactivity of Alcohols



- more substituted alcohol = more reactive
- increased reactivity = faster reaction
- remember: irreversible reaction; no equilibrium here

Higher Energy of Reactants = Increased Reactivity

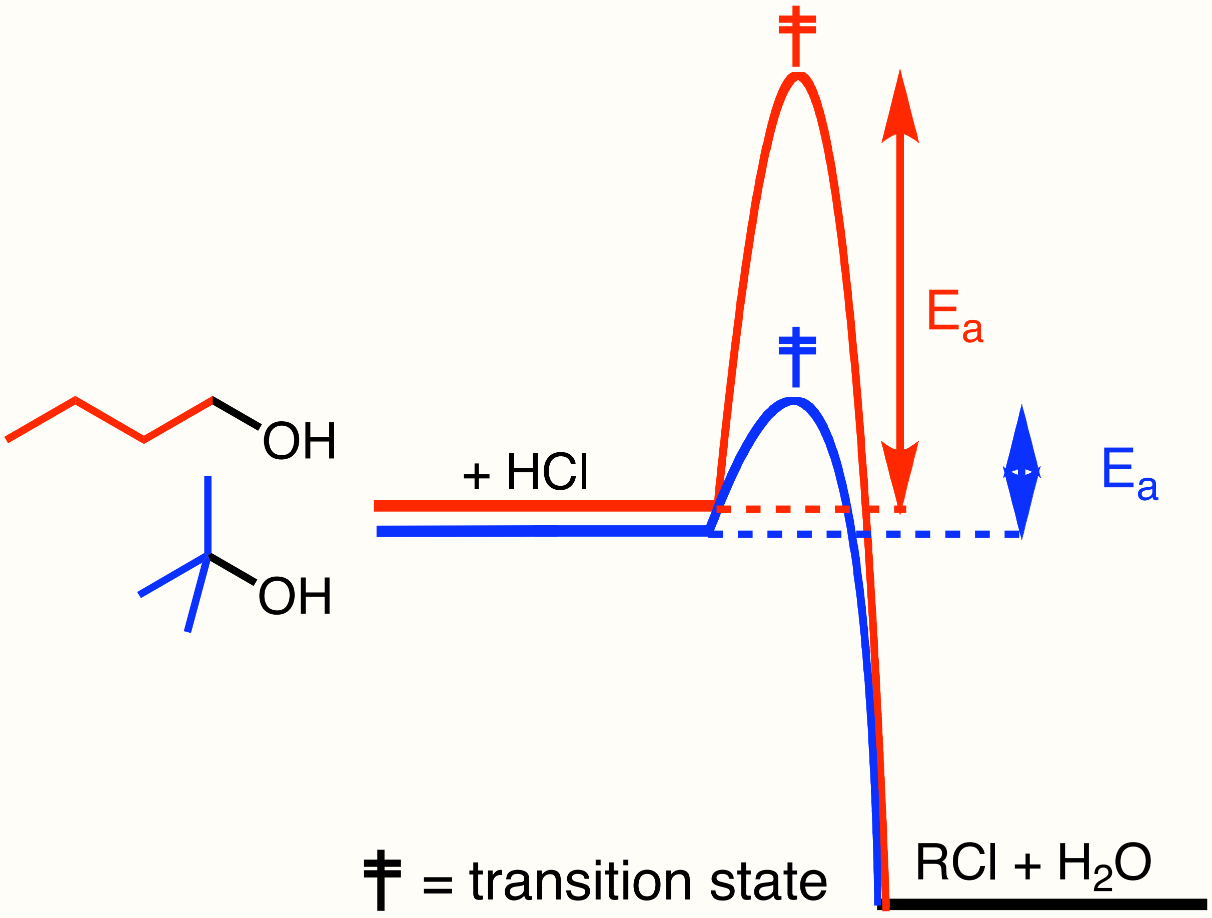


higher energy reactants =

if transition states are the same, then lower activation energy (Ea) =

faster reaction = more reactive

Lower Energy Transition States = Increased Reactivity



higher energy transition states =

if reactant energies are close, then lower activation energy (Ea) =

faster reaction
= more reactive

We will explore why 3° alcohols provide lower energy transition states on Thursday.

More Examples

$$(CH_3)_3COH + HCl \xrightarrow{25^\circ C} (CH_3)_3CCl + H_2O$$

2-Methyl-2-propanol (*tert*-butyl alcohol) | Hydrogen chloride | 2-Chloro-2-methylpropane (*tert*-butyl chloride) (78–88%) | Water

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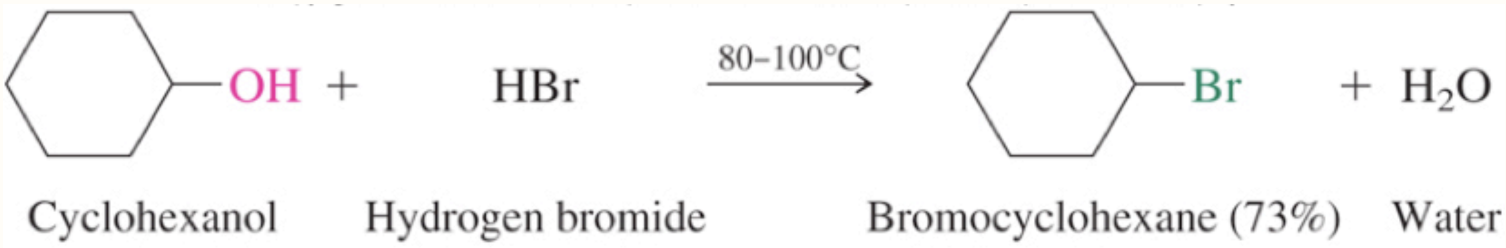


$$CH_3(CH_2)_5CH_2OH + HBr \xrightarrow{120^\circ C} CH_3(CH_2)_5CH_2Br + H_2O$$

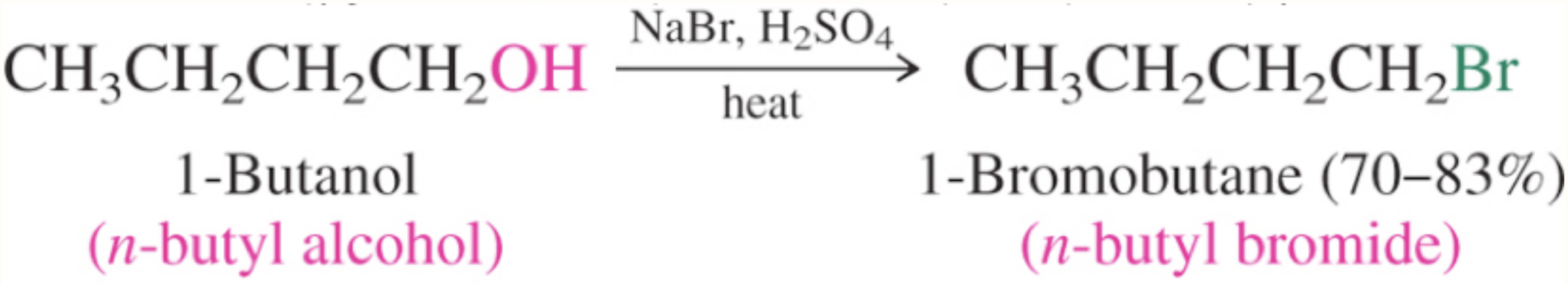
1-Heptanol | Hydrogen bromide | 1-Bromoheptane (87–90%) | Water

more reactive hydrogen halide (HBr) is needed for less reactive secondary alcohols

- think about the pattern of the reaction
- ignore parts of the molecule that don’t react
- reaction conditions: generally, above/below rxn arrow

Alternative Conditions

A mixture of sodium bromide and sulfuric acid may be used in place of HBr.



$$CH_3CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{NaBr, } H_2SO_4} CH_3CH_2CH_2CH_2Br$$

1-Butanol
(*n*-butyl alcohol)

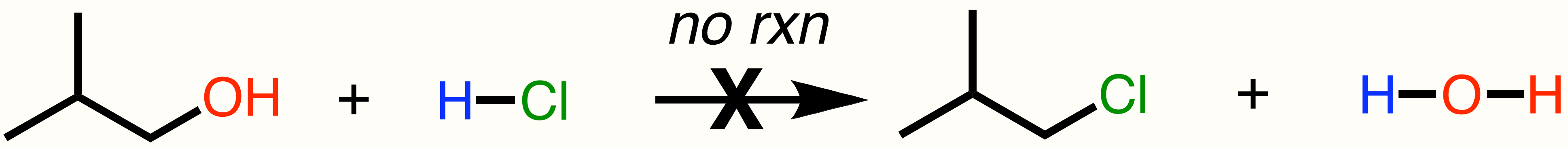
1-Bromobutane (70–83%)
(*n*-butyl bromide)

- reagents generally placed above/below reaction arrow
- inorganic products usually omitted (assumed)

1º & 2º Alcohols Unreactive Toward HCl

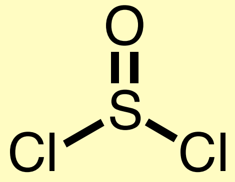
$$(CH_3)_3COH + HCl \xrightarrow{25°C} (CH_3)_3CCl + H_2O$$

2-Methyl-2-propanol (*tert*-butyl alcohol) + Hydrogen chloride → 2-Chloro-2-methylpropane (*tert*-butyl chloride) (78–88%) + Water

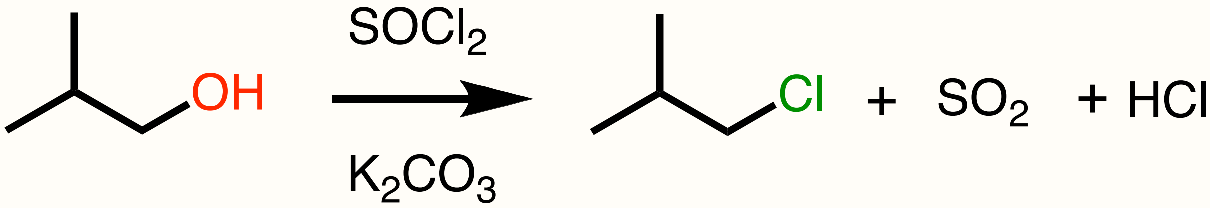


Alternative Reagent for Preparation of Alkyl Chlorides

thionyl chloride

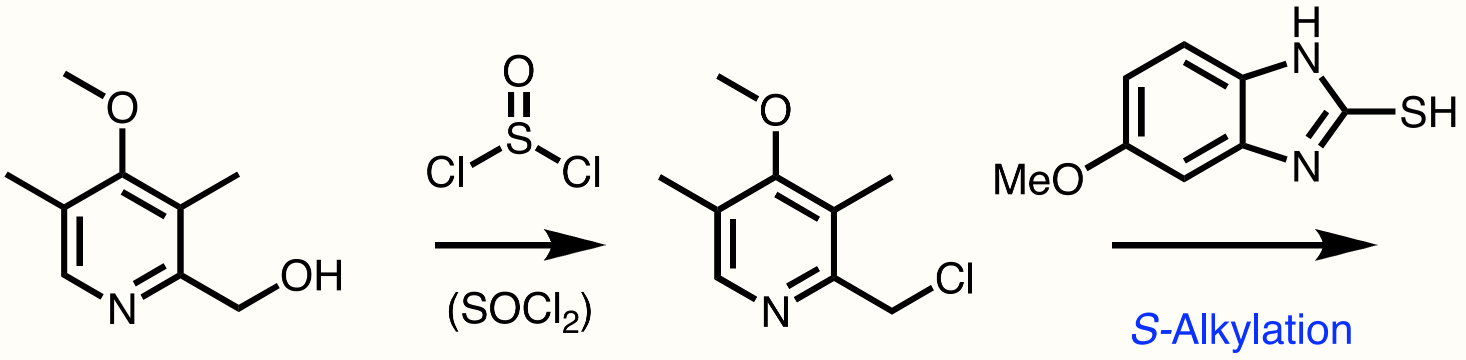


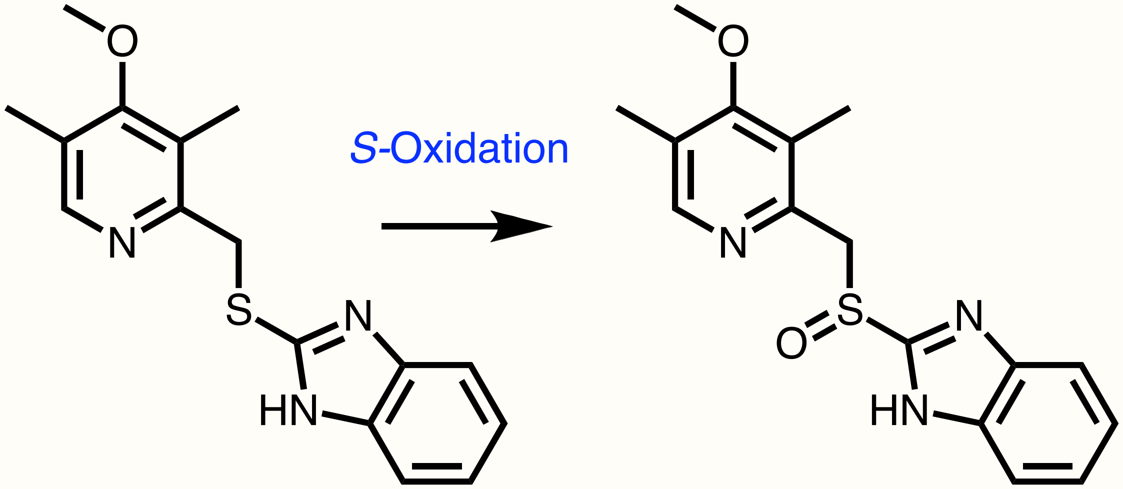
$SOCl_2$



- thionyl chloride reacts rapidly with 1º and 2º alcohols
- byproducts of the reaction are SO_2(g) and HCl(g)
- base is needed to neutralize HCl: e.g. K_2CO_3, pyridine

Alkyl Halides & Purple Pills



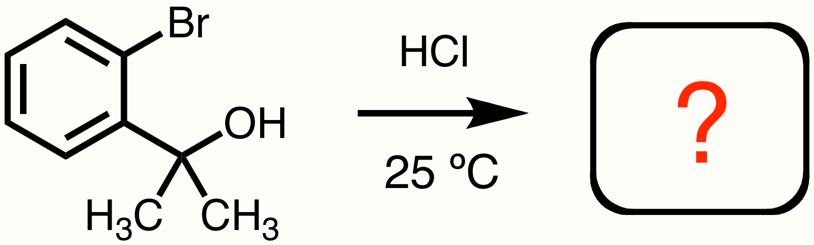


Esomeprazole

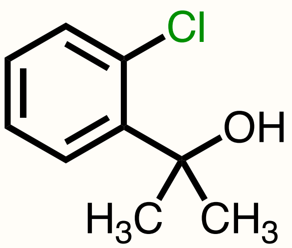
Nexium®

Self Test Question

Predict the organic product of the following reaction...



a.



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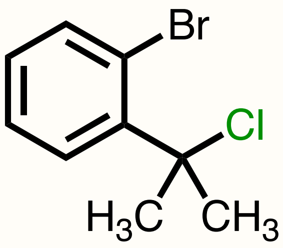
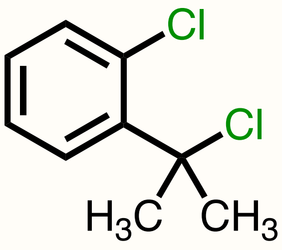
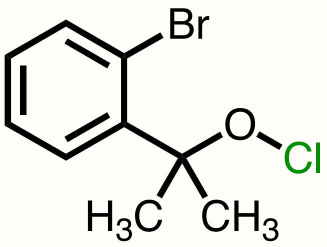


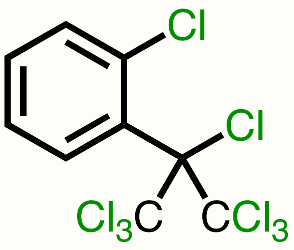
c.



d.



e.



A. a

B. b

C. c

D. d

E. e

Next Lecture. . .

Chapter 4: Sections 4.9-4.18

Quiz This Week

- Topic = Chapter 3
- Conformational Analysis of *n*-Alkanes
- Conformations of Cyclohexane
- Cyclohexane Ring Inversion
- Conformational Analysis of Mono & Disubstituted Cyclohexanes
- Bring a Calculator to Discussion!