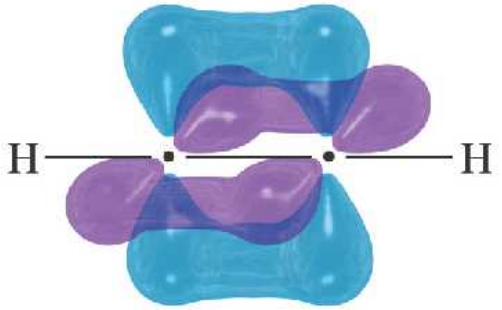
DAMIETTA UNIVERSITY

CHEM-103:

BASIC ORGANIC CHEMISTRY

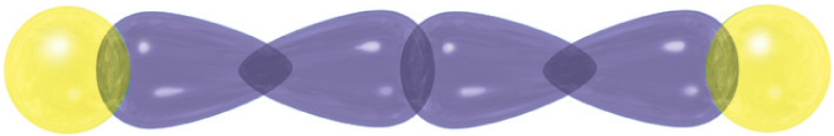
LECTURE 6

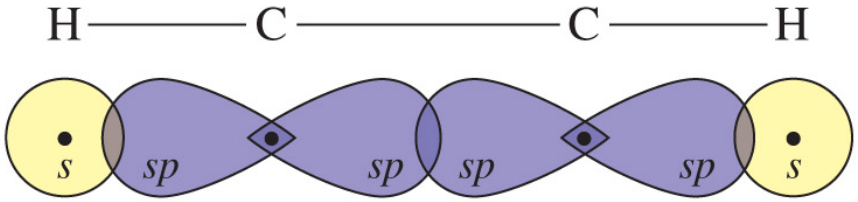
Dr Ali El-Agamey



Alkynes

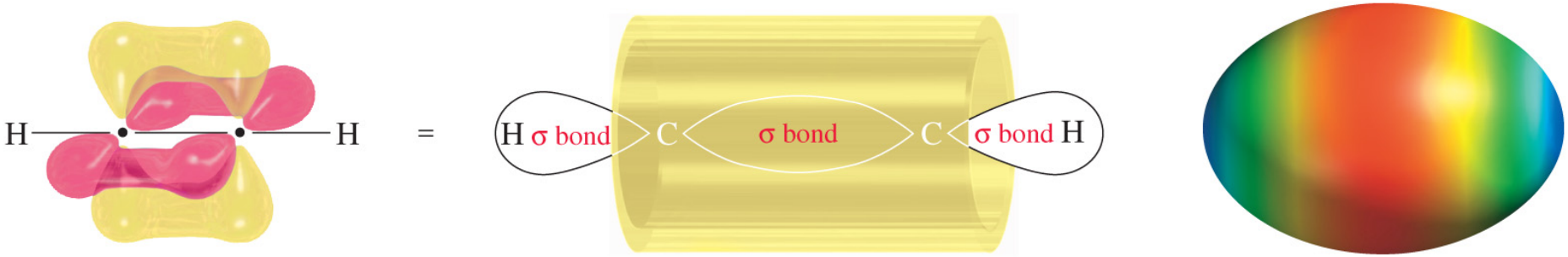
Molecular Structure of Acetylene





- Triple-bonded carbons have ***sp* hybrid orbitals**.
- A sigma bond is formed between the carbons by overlap of the *sp* orbitals.
- Sigma bonds to the hydrogens are formed by using the second *sp* orbital.
- Since the *sp* orbitals are linear, acetylene will be a **linear molecule**.

Overlap of the *p* Orbitals of Acetylene



overlap of *p* orbitals

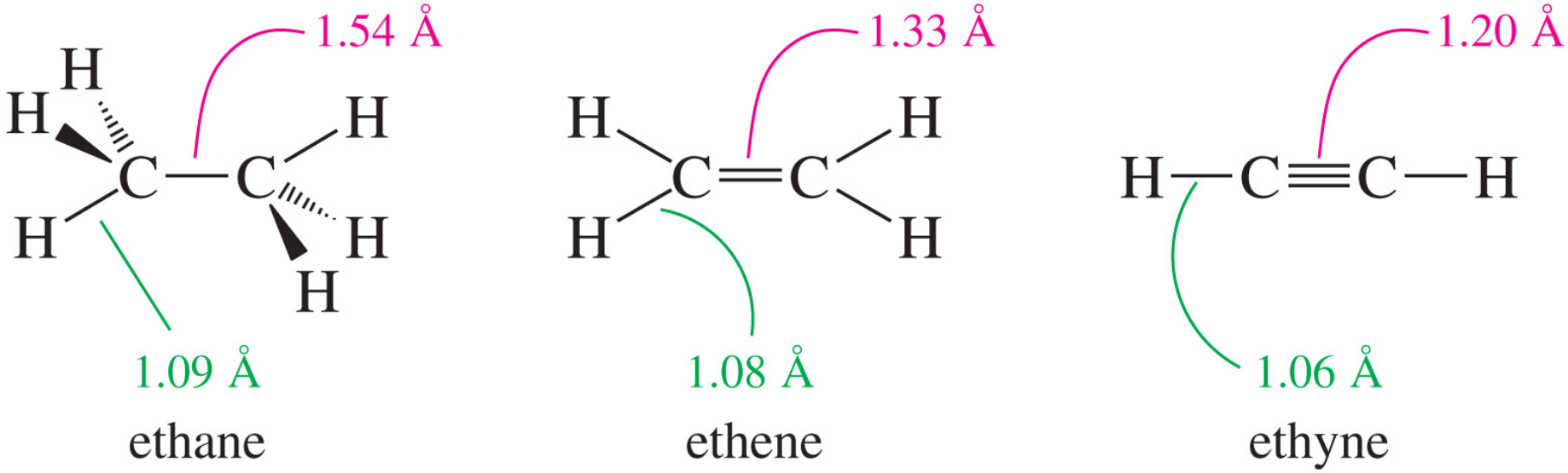
cylinder of electron density

EPM of acetylene

Each carbon in acetylene has two unhybridized *p* orbitals with one nonbonded electron. It is the overlap of the **parallel** *p* orbitals that form the triple bond (**2 pi orbitals**).

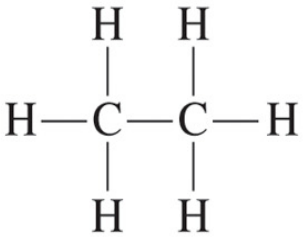
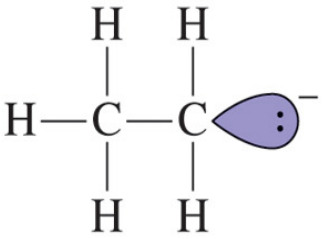
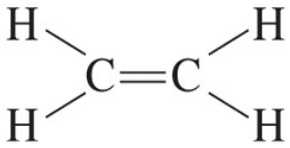
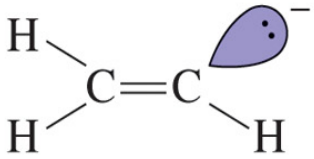
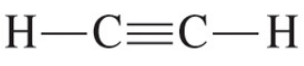
Bond Lengths

- Triple bonds are **shorter** than double or single bonds because of the two pi overlapping orbitals.

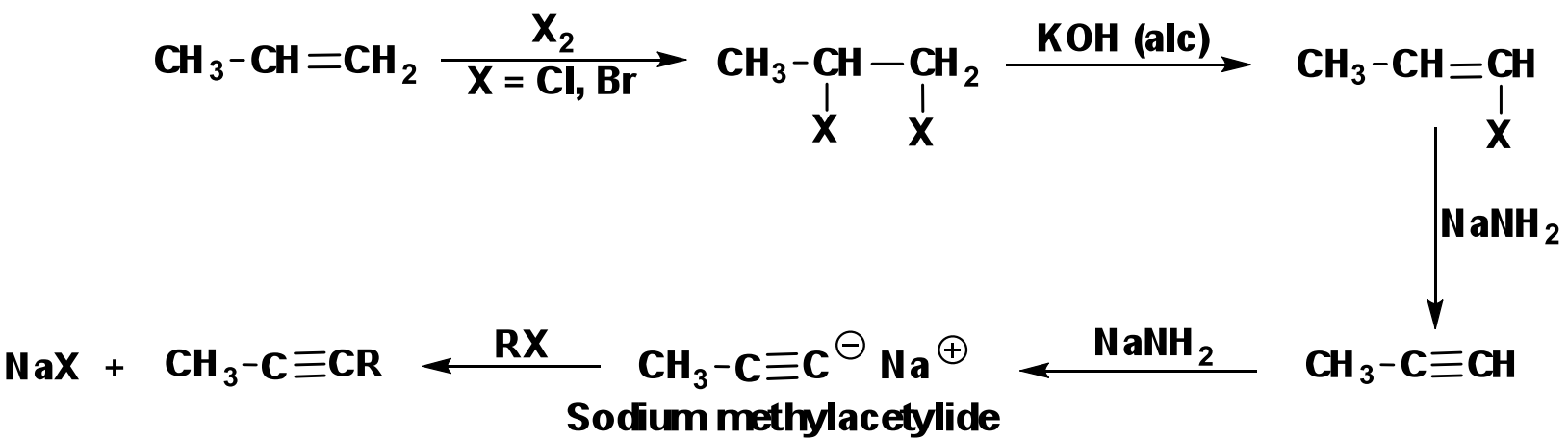


Acidity Table

TABLE 9-2

Compound	Conjugate Base	Hybridization	*s* Character	pK_a	
		sp^3	25%	50	weakest acid
		sp^2	33%	44	
$:NH_3$	$:\ddot{N}H_2^-$	(ammonia)		35	
		sp	50%	25	
R—OH	R—$\ddot{O}:^-$	(alcohols)		16–18	stronger acid

Preparation of Alkynes



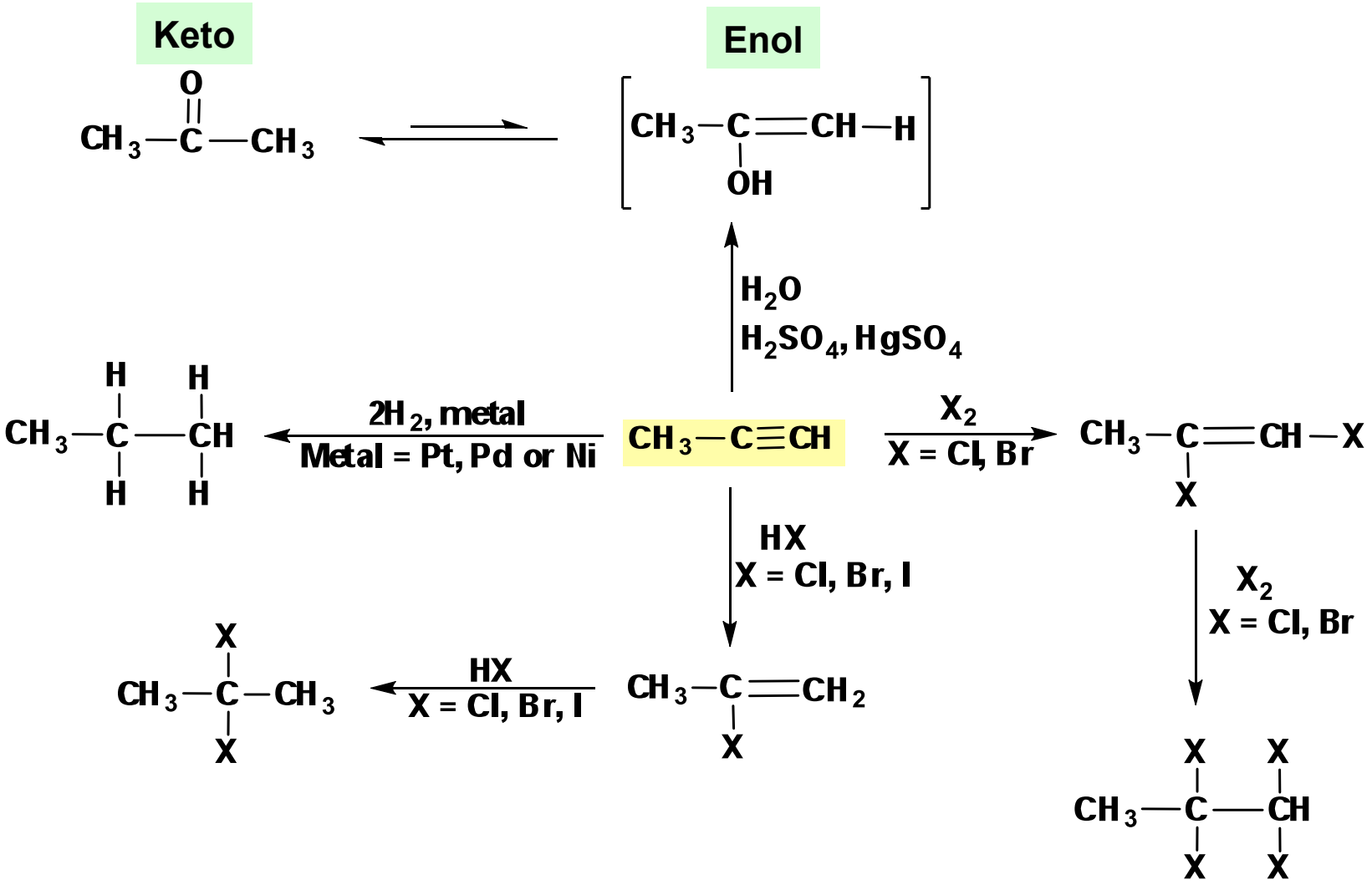
RX must be 1°

Propyne

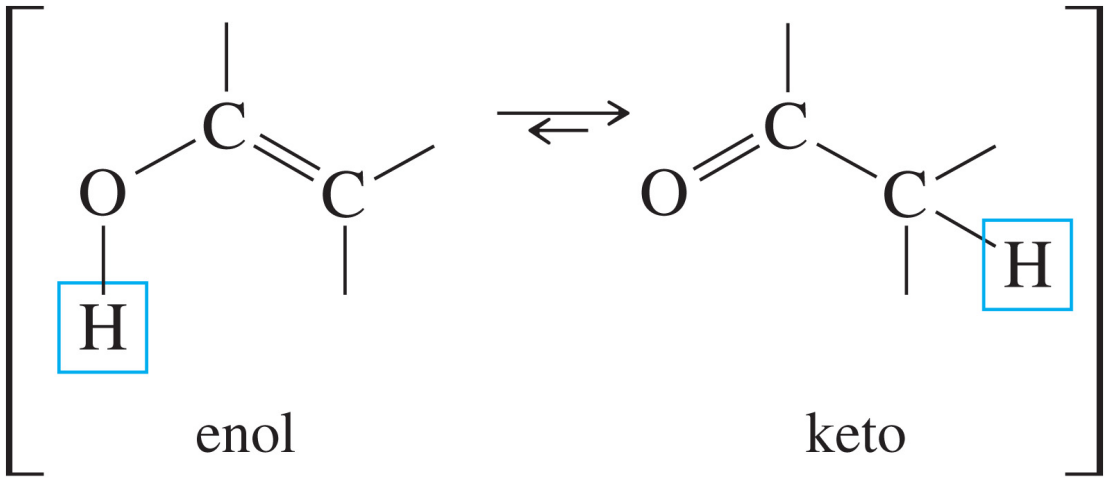
Pent-2-yne

$NaNH_2$: Sodium amide

Reactions of Alkynes



Keto–Enol Tautomerism

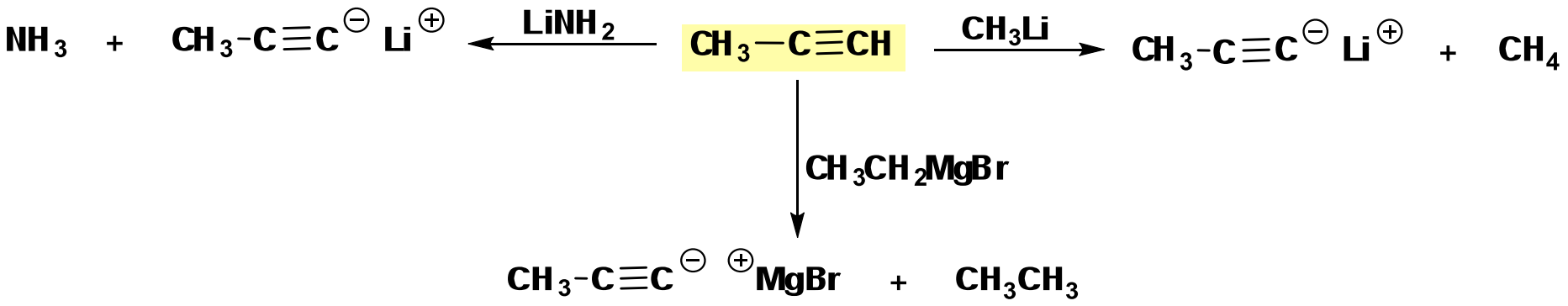


keto–enol tautomerism

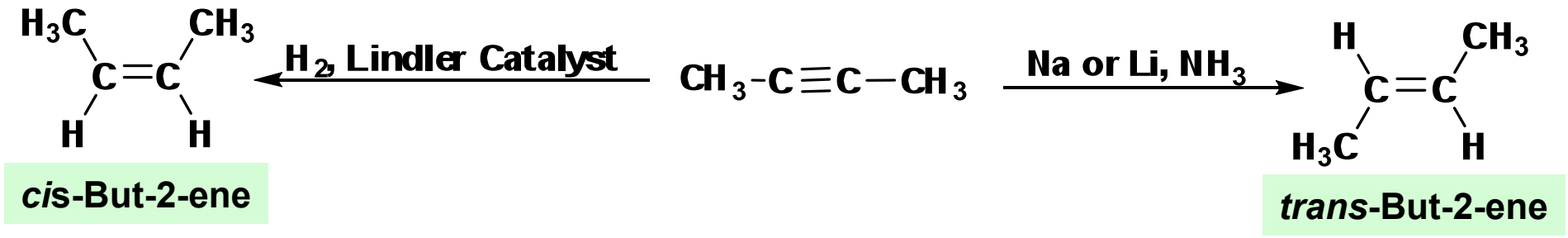
- **Tautomers:** are compounds whose structures **differ** markedly **in arrangement of atoms**, but which exist in easy and **rapid equilibrium**.[1]
- **Enols are not stable** and they isomerize to the corresponding aldehyde or ketone in a process known as **keto-enol tautomerism**.

Reactions of Alkynes

Reactions as acids



Reduction to Alkenes



cis-But-2-ene

trans-But-2-ene

Homework

9.26 Write the structure of the major organic product isolated from the reaction of 1-hexyne with

(a) Hydrogen (2 mol), platinum

(b) Hydrogen (1 mol), Lindlar palladium

(c) Lithium in liquid ammonia

(d) Sodium amide in liquid ammonia

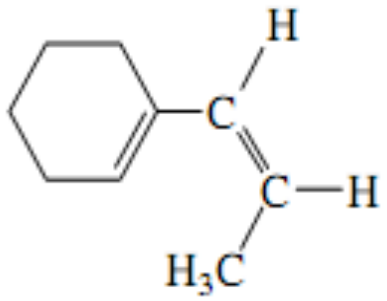
(e) Product in part (d) treated with 1-bromobutane

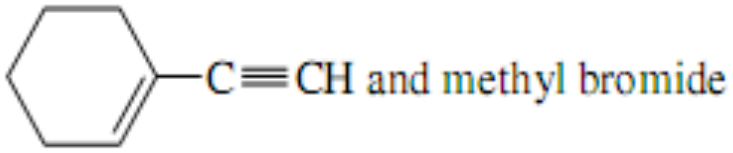
Homework

9.33 Show by writing a suitable series of equations how you could prepare each of the following compounds from the designated starting materials and any necessary organic or inorganic reagents:

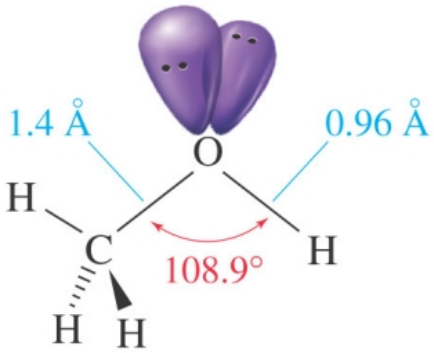
(a) 2,2-Dibromopropane from 1,1-dibromopropane

(f) Decane from 1-butene and acetylene

(h) 

from 

and methyl bromide

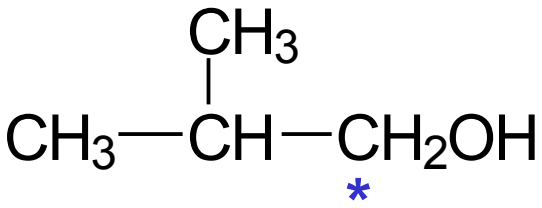


Alcohols

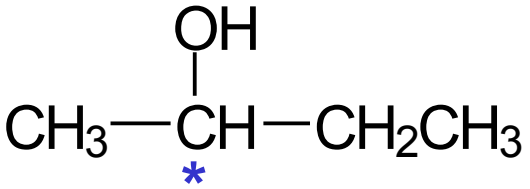
Classification of Alcohols

- Primary: carbon with —OH is bonded to one other carbon.
- Secondary: carbon with —OH is bonded to two other carbons.
- Tertiary: carbon with —OH is bonded to three other carbons.
- Aromatic (phenol): —OH is bonded to a benzene ring.

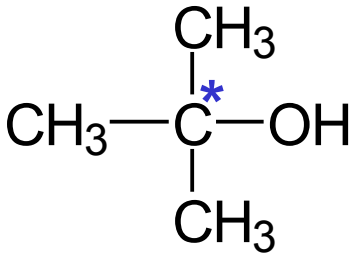
Examples of Classifications



Primary alcohol

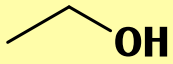


Secondary alcohol

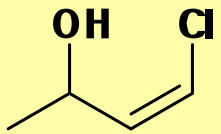


Tertiary alcohol

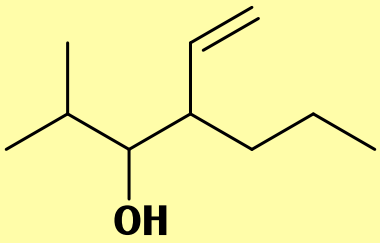
Homework: Write the IUPAC name of the following compounds



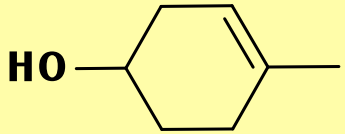
(a)



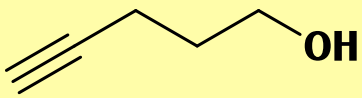
(e)



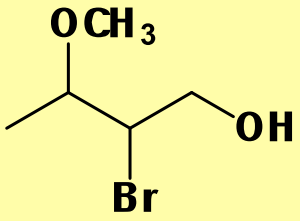
(f)



(h)

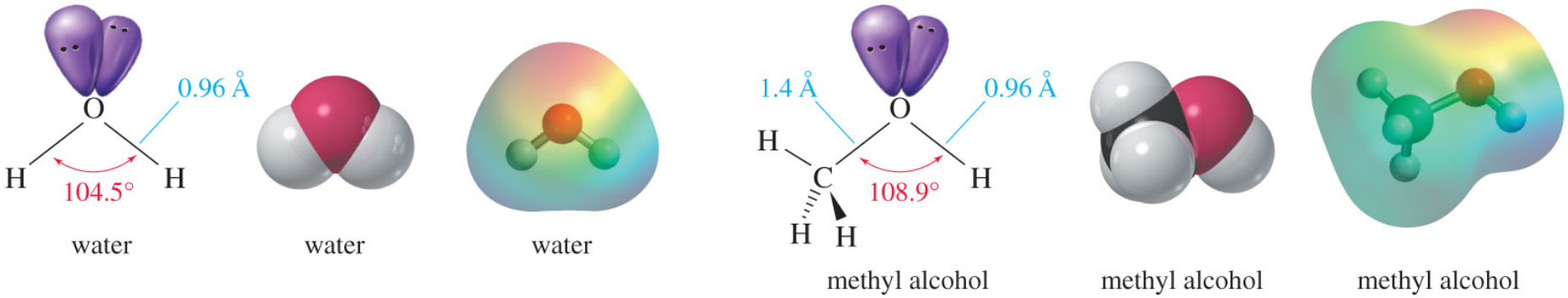


(j)



(k)

Structure of Water and Methanol



- Oxygen is sp^3 hybridized and tetrahedral.
- The H—O—H angle in water is 104.5°.
- The C—O—H angle in methyl alcohol is 108.9°.

Physical Properties

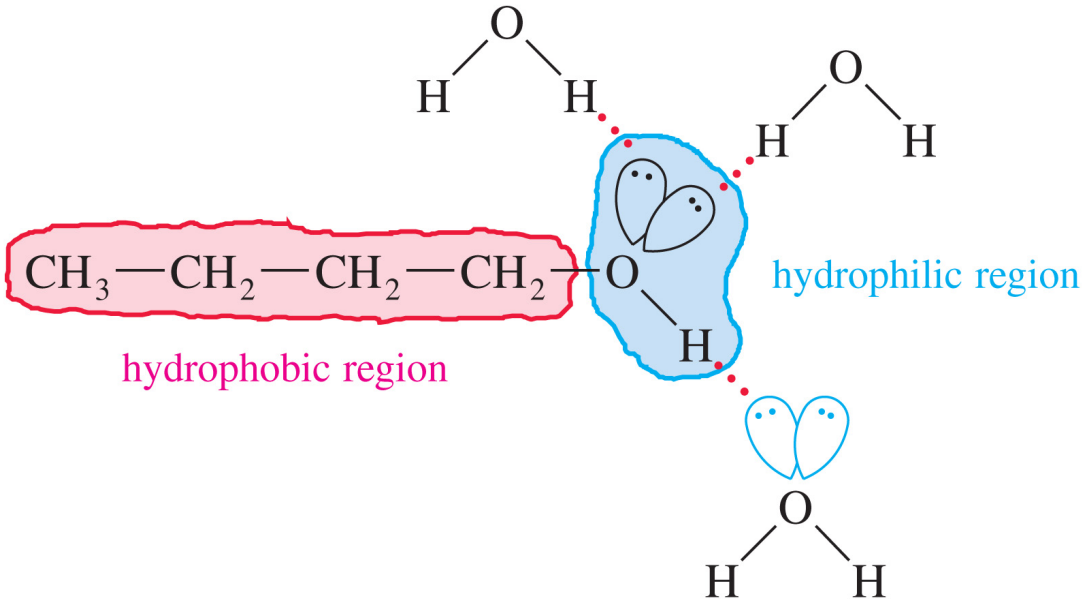
- Alcohols have **high boiling points** due to **hydrogen bonding** between molecules.
- Small alcohols are **miscible** in water, but solubility decreases as the size of the alkyl group increases.

Solubility in Water

TABLE 10-3

Solubility of Alcohols in Water (at 25 °C)

Alcohol	Solubility in Water
methyl	miscible
ethyl	miscible
n-propyl	miscible
t-butyl	miscible
isobutyl	10.0%
n-butyl	9.1%
n-pentyl	2.7%
cyclohexyl	3.6%
n-hexyl	0.6%
phenol	9.3%
hexane-1,6-diol	miscible

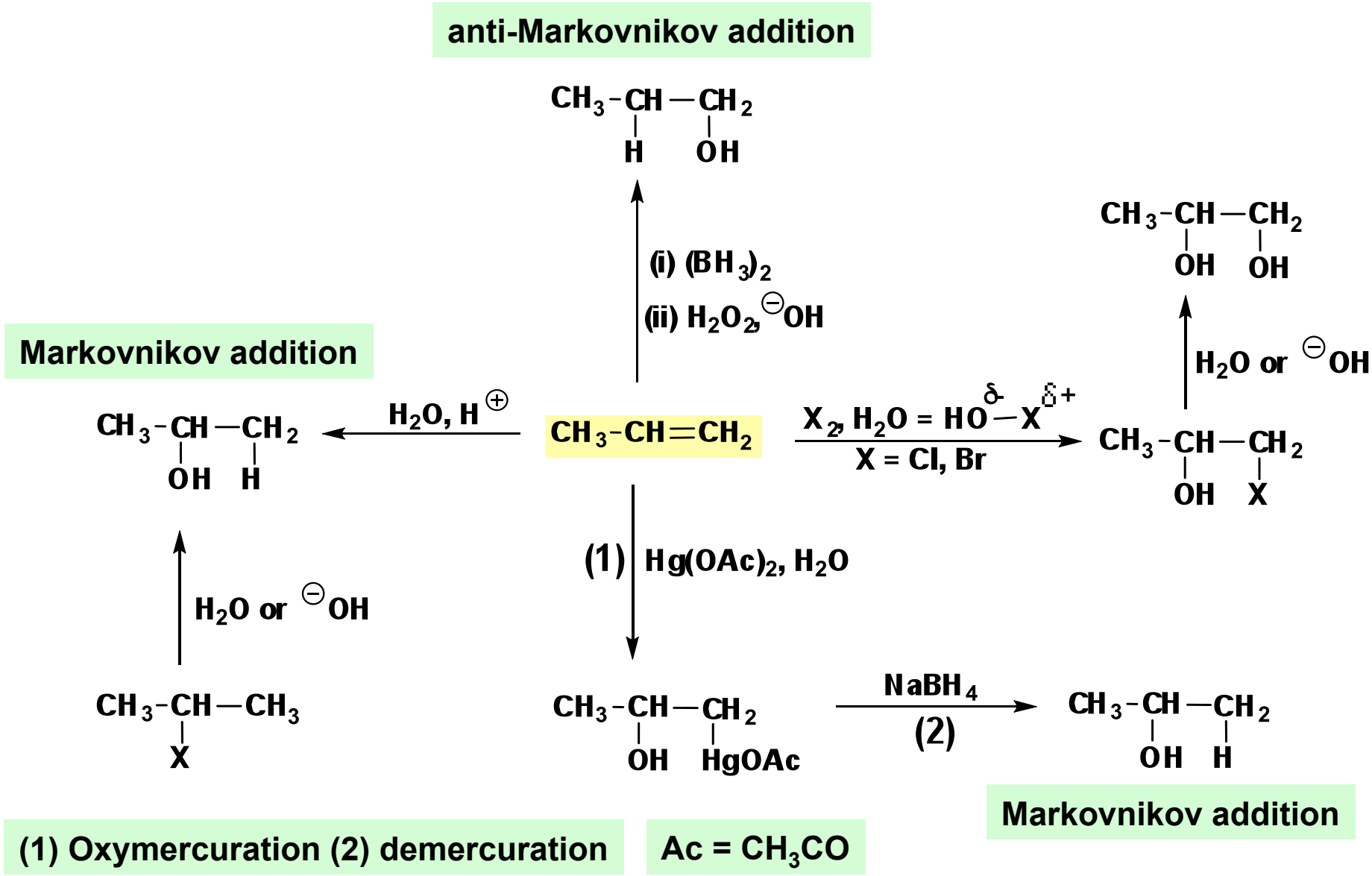


Small alcohols are miscible in water, but as the size of the alkyl group **(hydrophobic)** increases, solubility with water **(polar solvent)** decreases.

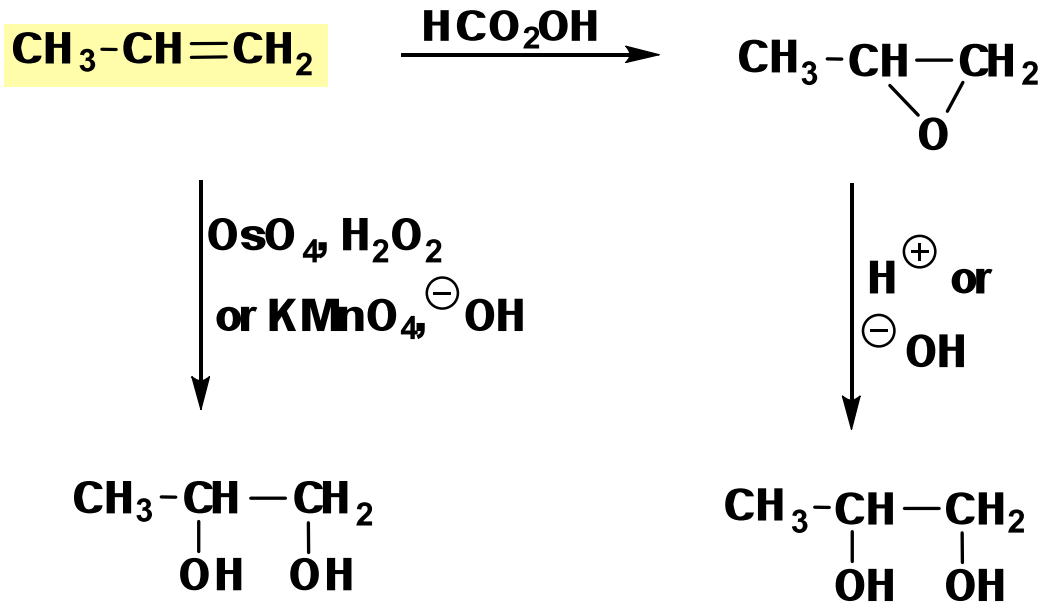
Solubility in Water

- If a molecule is big enough (e.g. chain of 16 to 20 carbons), the hydrophilic parts dissolve in water and the **hydrophobic parts cluster together**. Such dual solubility behavior gives soaps and detergents their cleaning power.[1]

Preparation of Alcohols



Preparation of Alcohols



Grignard Reagents

$$R{-}X + Mg \xrightarrow{CH_3CH_2OCH_2CH_3} \overset{\delta^-}{R}{-}\overset{\delta^+}{Mg}{-}X$$

(X = Cl, Br, or I)

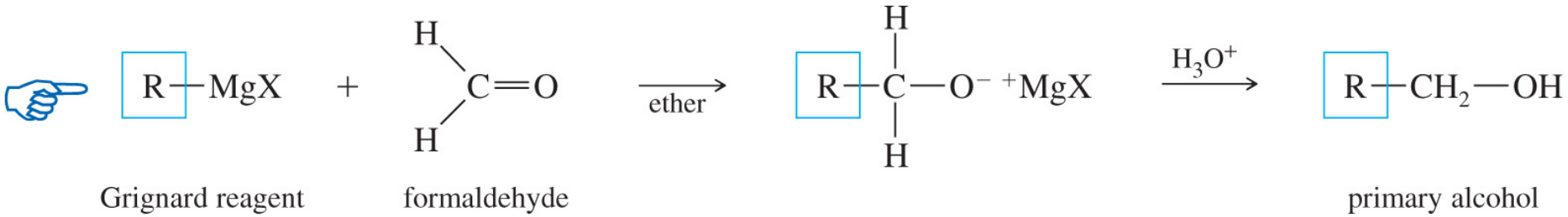
organomagnesium halide
(Grignard reagent)

reacts like $R:^- \overset{+}{M}gX$

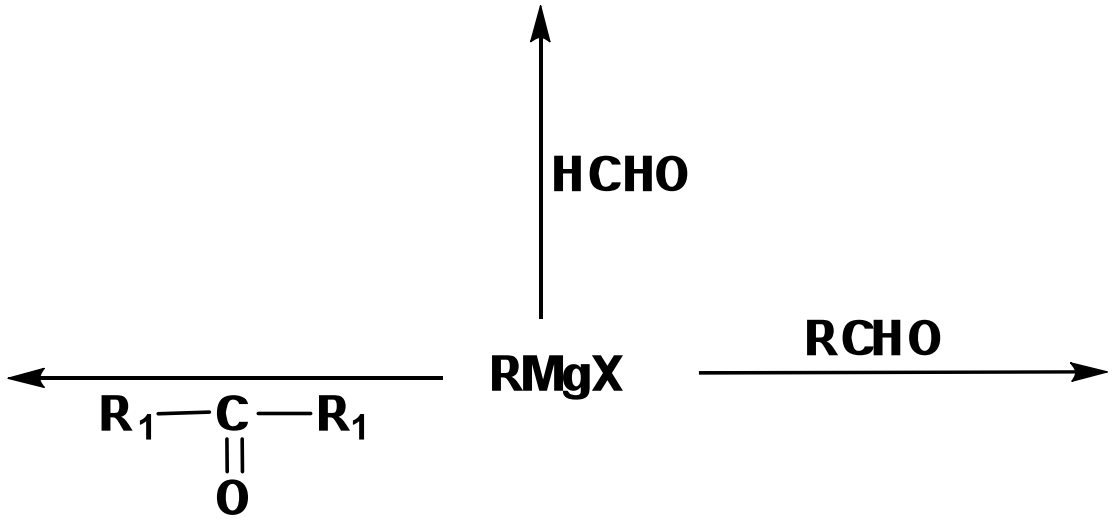
- Formula R—Mg—X (reacts like $R:^- {}^+MgX$).
- Ethers are used as solvents to stabilize the complex.
- May be formed from **any** halide.

Examples

Reaction with Carbonyl



Preparation of Alcohols



How could you prepare the following compound by three different methods?