

CHM 138 H

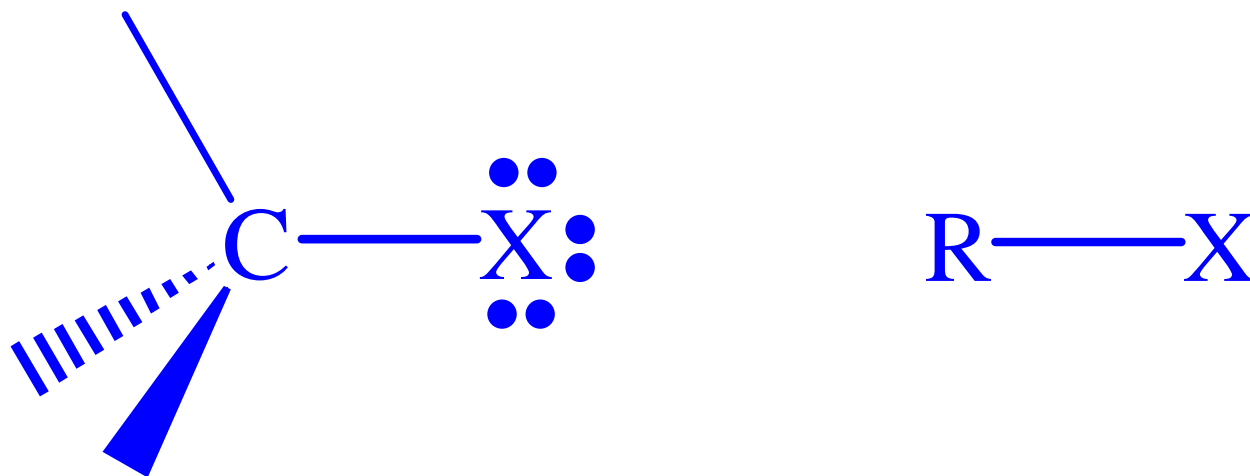
The Chemistry of the Alkyl Halides

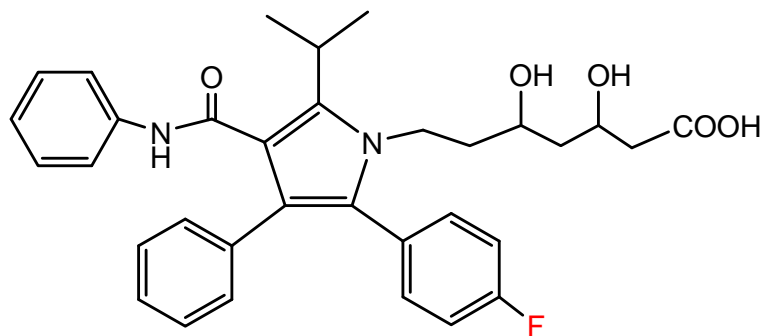
Chapter 10, excluding 10.2, 10.3, 10.4,
10.7 (only Gilman Reactions)

Based on McMurry, 8th Edn.

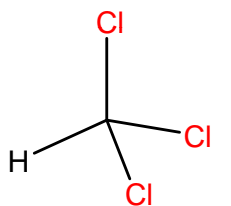
STRUCTURE OF ALKYL HALIDES

Alkyl halide: a compound containing a halogen atom covalently bonded to an ___ hybridized carbon atom

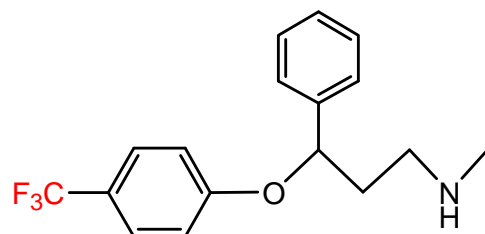




Lipitor



Chloroform



Prozac

Lipitor lowers blood cholesterol by inhibiting a liver enzyme that produces cholesterol.

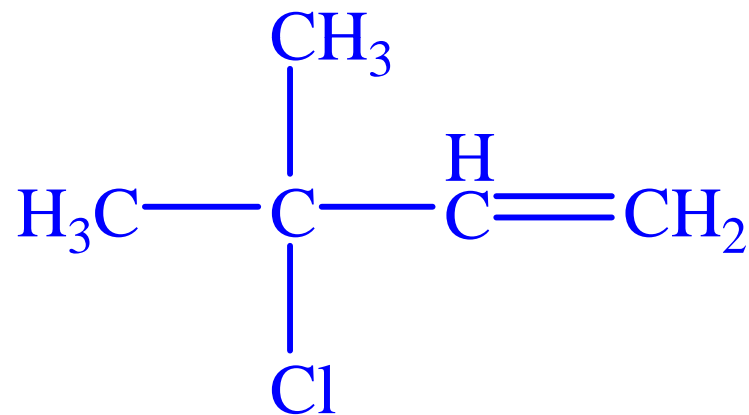
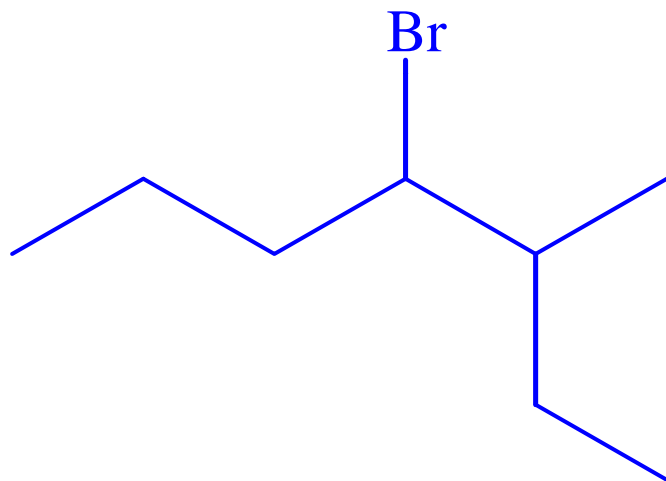
(The best selling drug in pharmaceutical history, sales of Lipitor since it was approved in 1996 exceed US\$125 billion)

Prozac is an widely used antidepressant that affects the metabolism of the neurotransmitter serotonin

Chloroform is colorless, sweet-smelling, dense liquid. Was once used as an anesthetic, now a common solvent and reagent

NOMENCLATURE

Halogen substituents are indicated by the prefixes fluoro-, chloro-, bromo-, and iodo- and listed in alphabetical order with other substituents

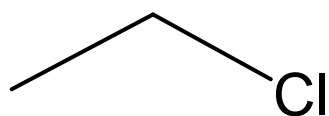


Common names - the name of the hydrocarbon group is followed by the name of the halide



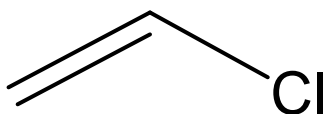
chloroethane

_____ chloride



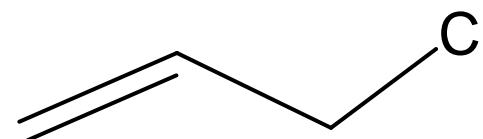
chloroethene

_____ chloride

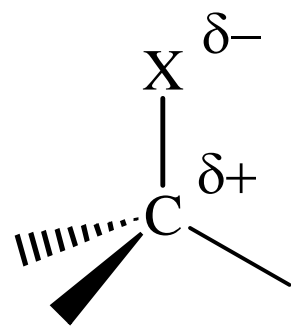


3-chloropropene

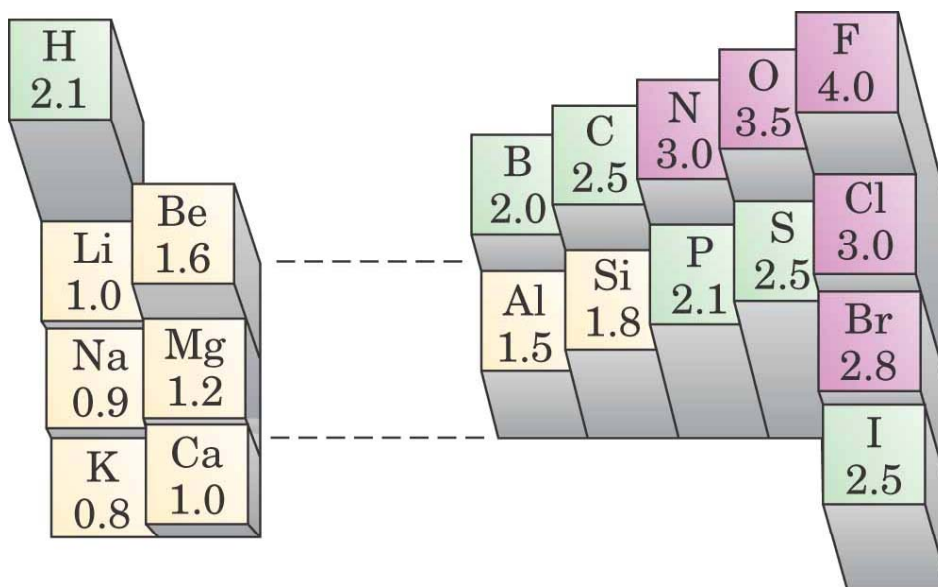
_____ chloride



PROPERTIES OF ALKYL HALIDES



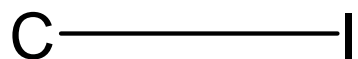
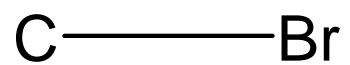
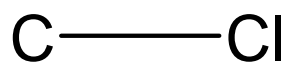
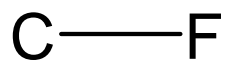
X=F, Cl, Br, I



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Bond length

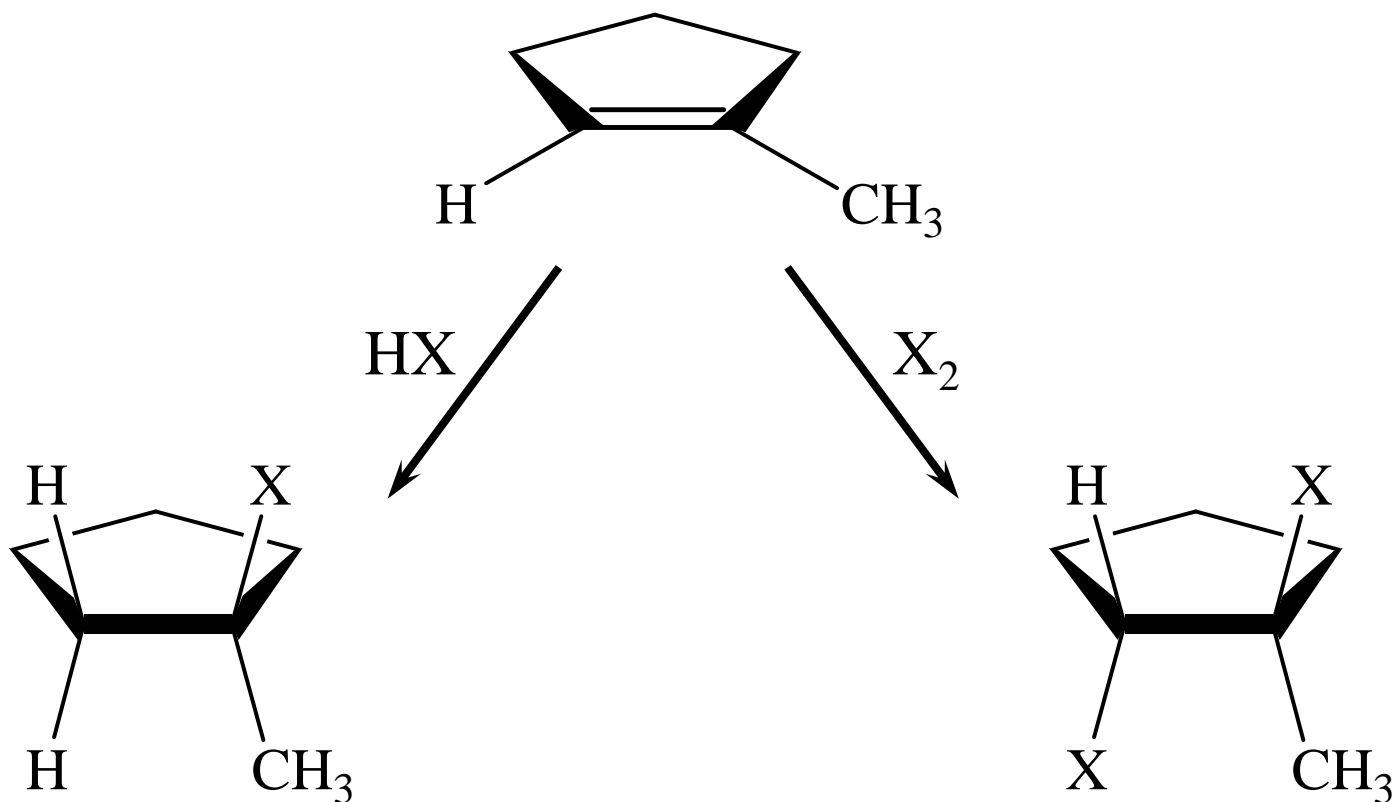
Bond Strength



Preparation of alkyl halides

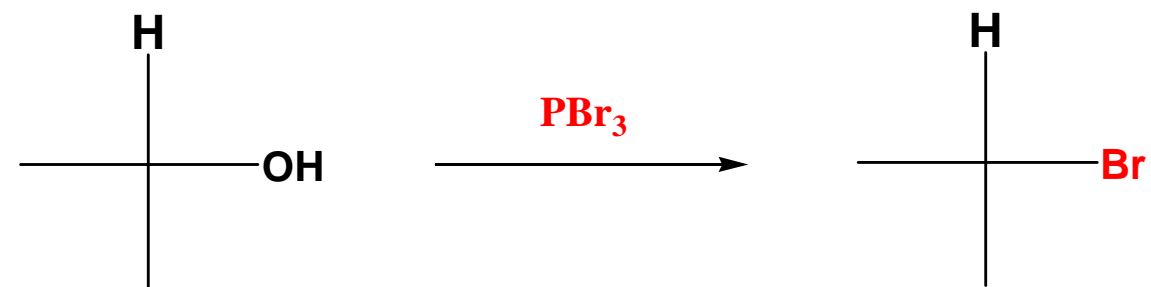
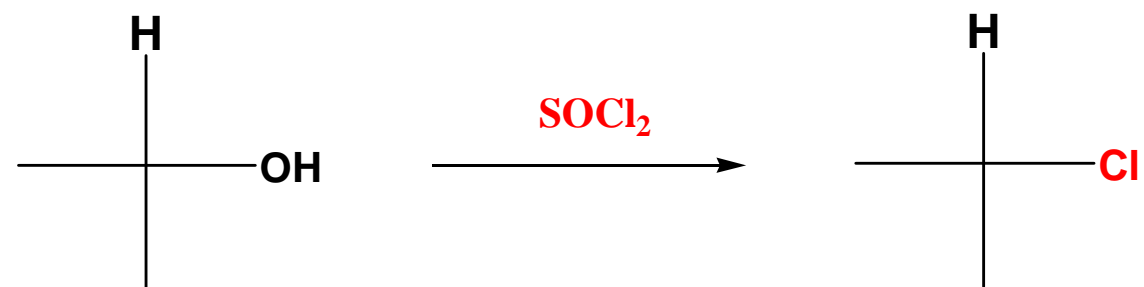
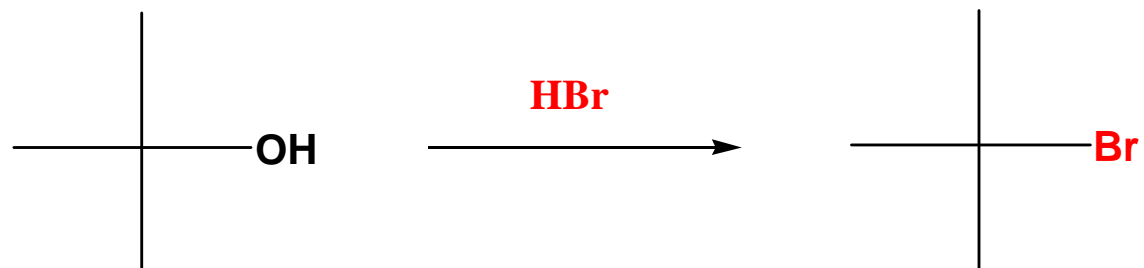
- 1) REACTION OF ALKENES WITH HX OR X₂
- 2) FROM ALCOHOLS

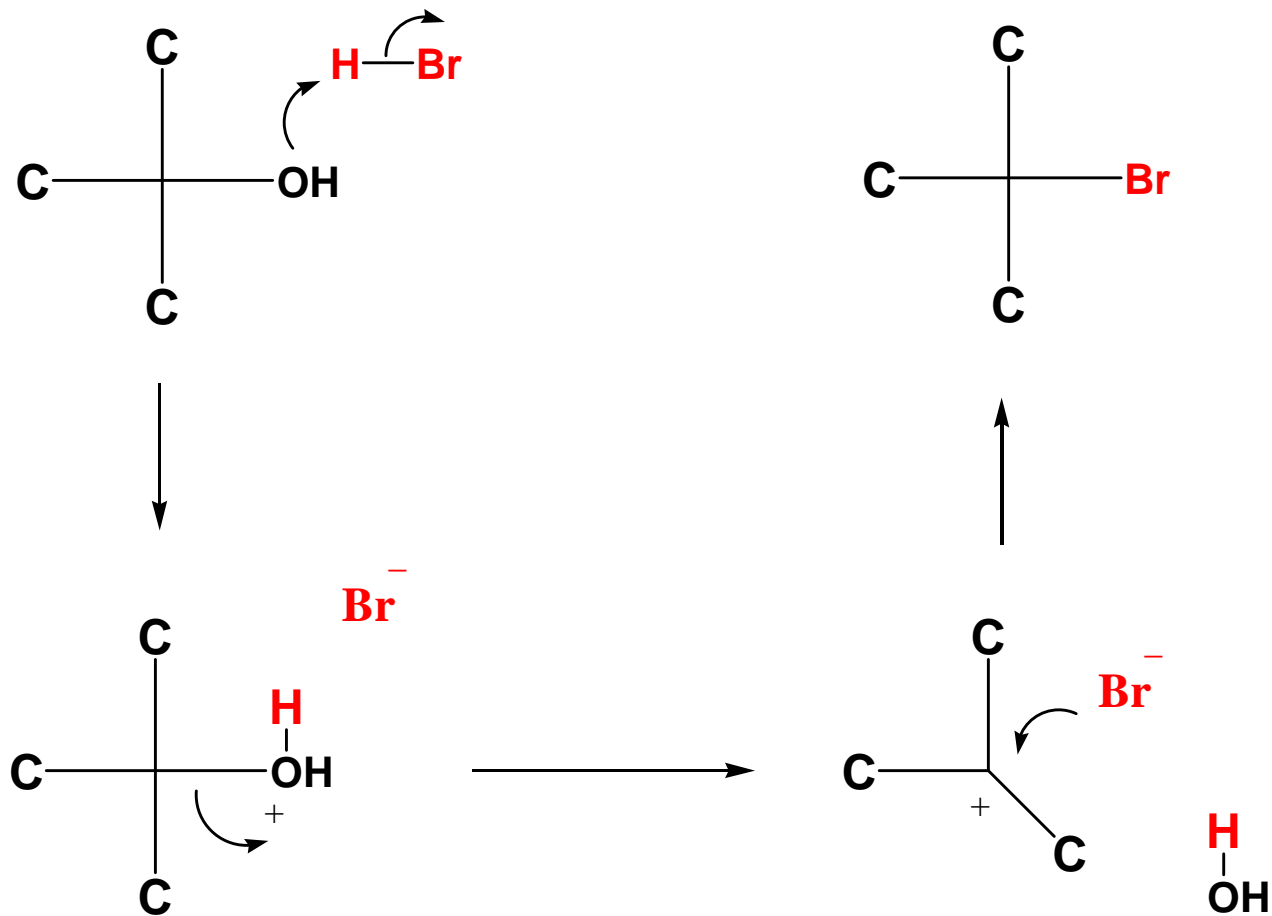
REACTION OF ALKENES WITH HX OR X₂



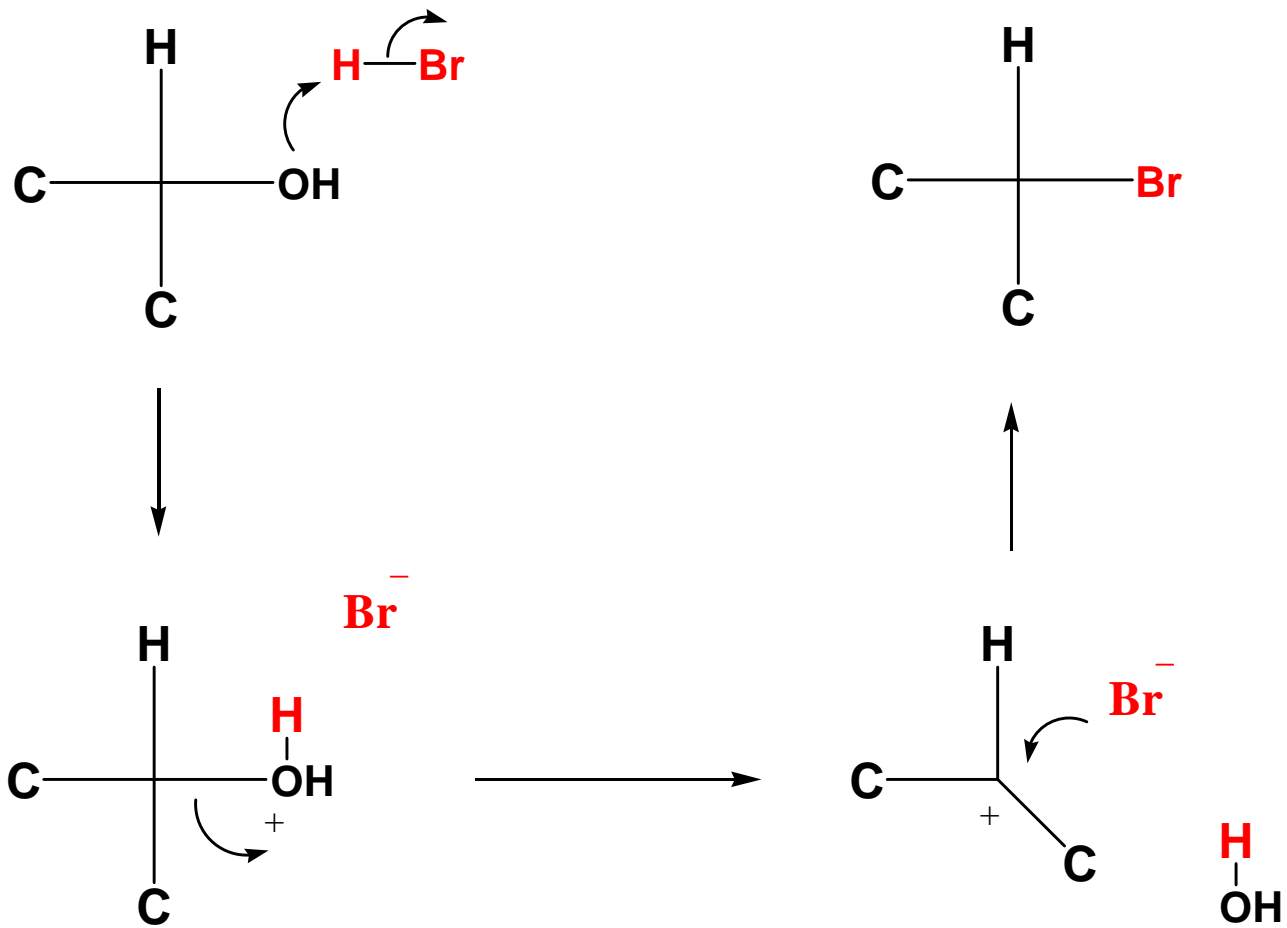
Review

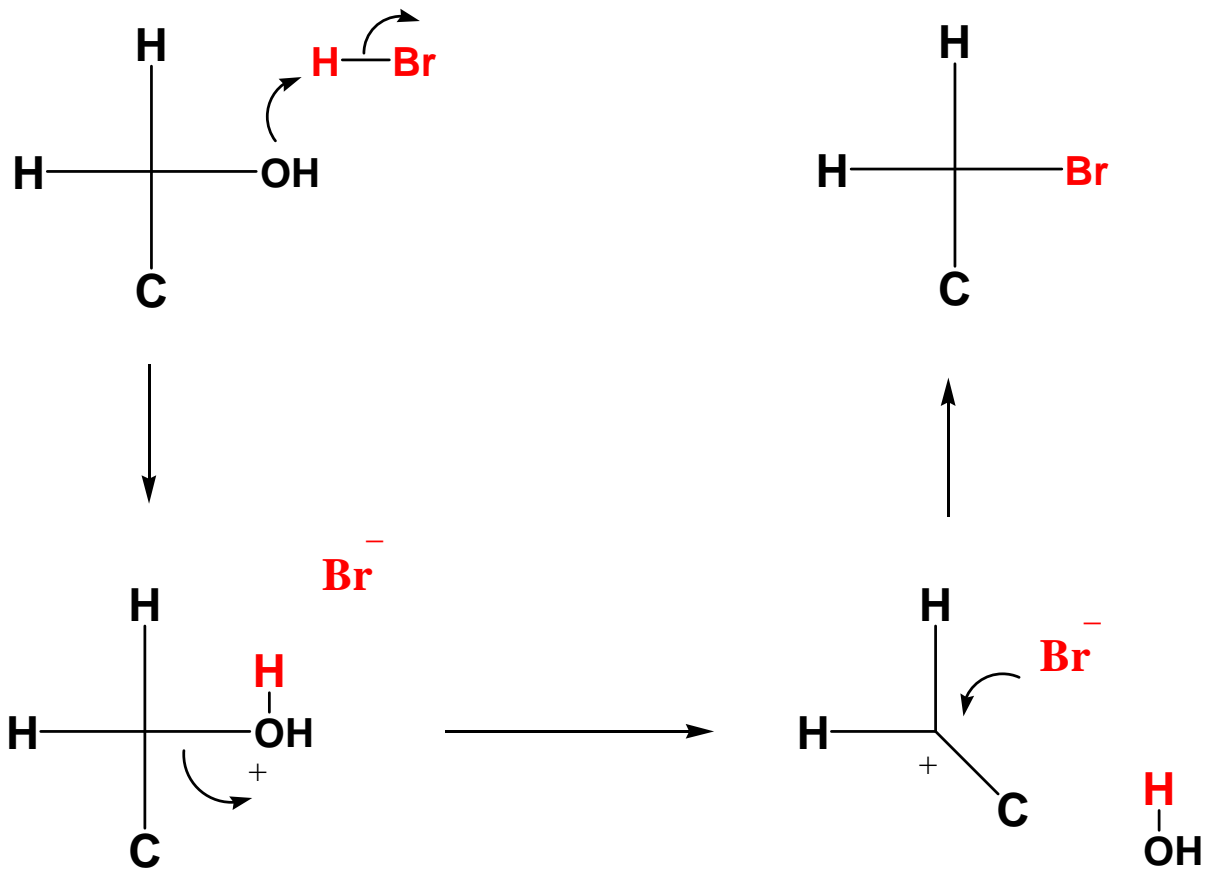
ALKYL HALIDES FROM ALCOHOLS





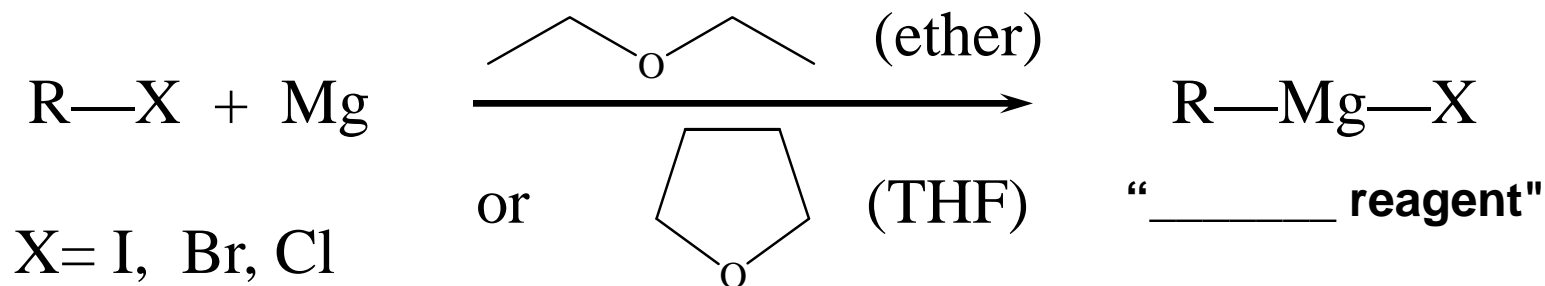
$3^{\circ} > 2^{\circ} > 1^{\circ}$



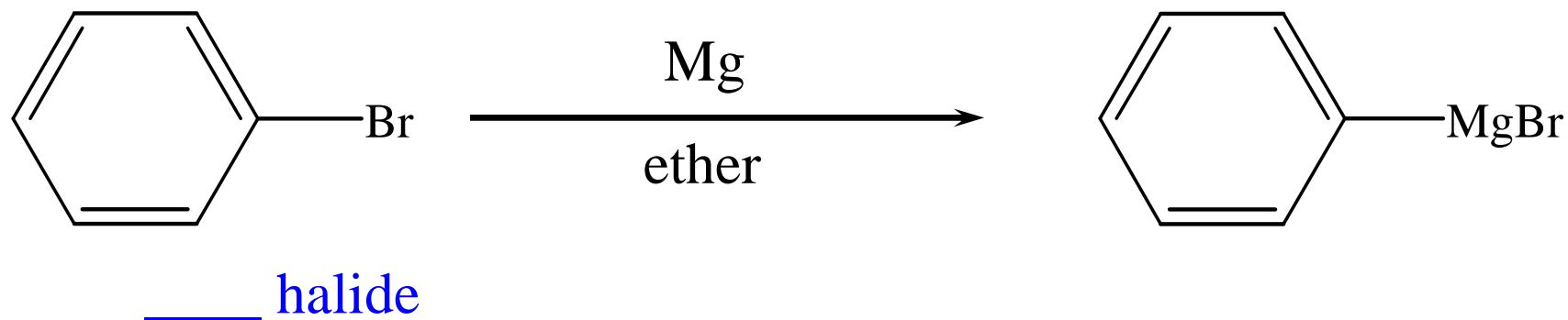
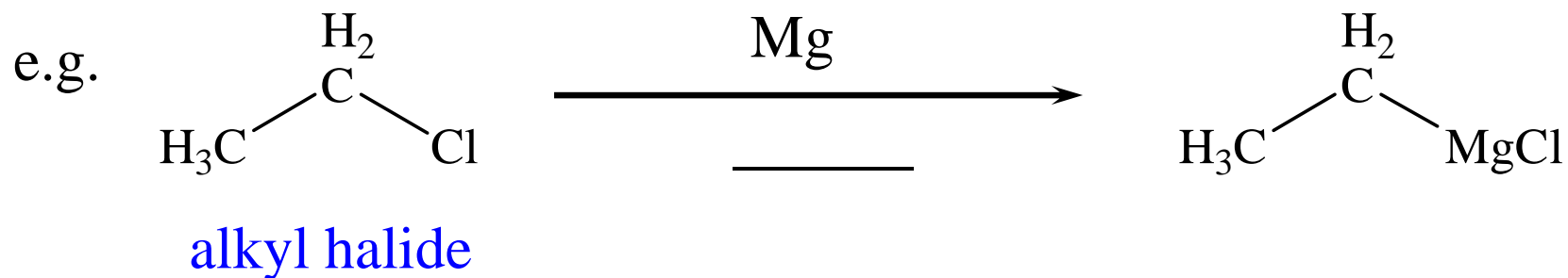


$3^{\circ} > 2^{\circ} > 1^{\circ}$

The Grignard reaction:

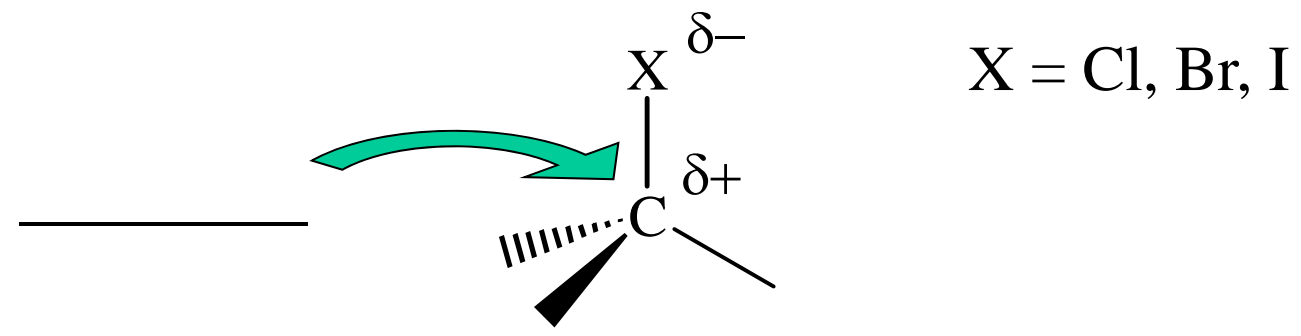


Is quite general:

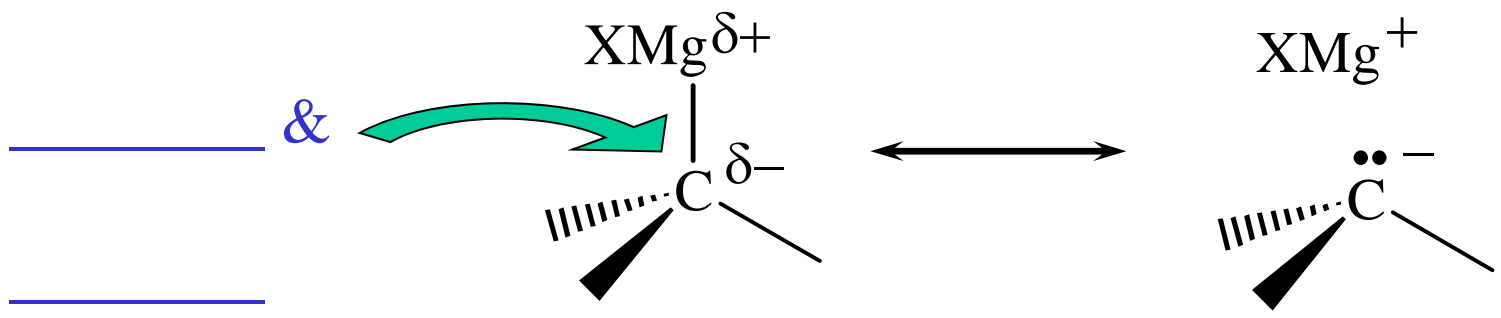


GRIGNARD REAGENTS: "organomagnesium halides"

recall:

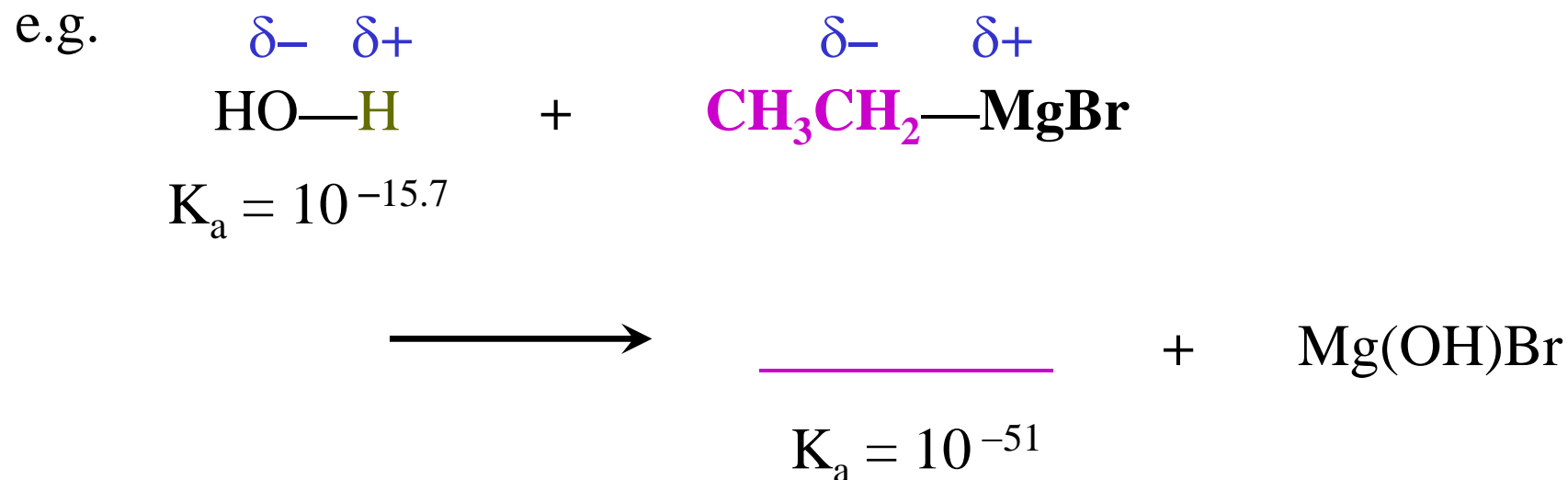


compare to:



REACTIONS OF GRIGNARD REAGENTS

(a) Reactions with "acids":



Classes of proton donors that react with Grignard reagents:

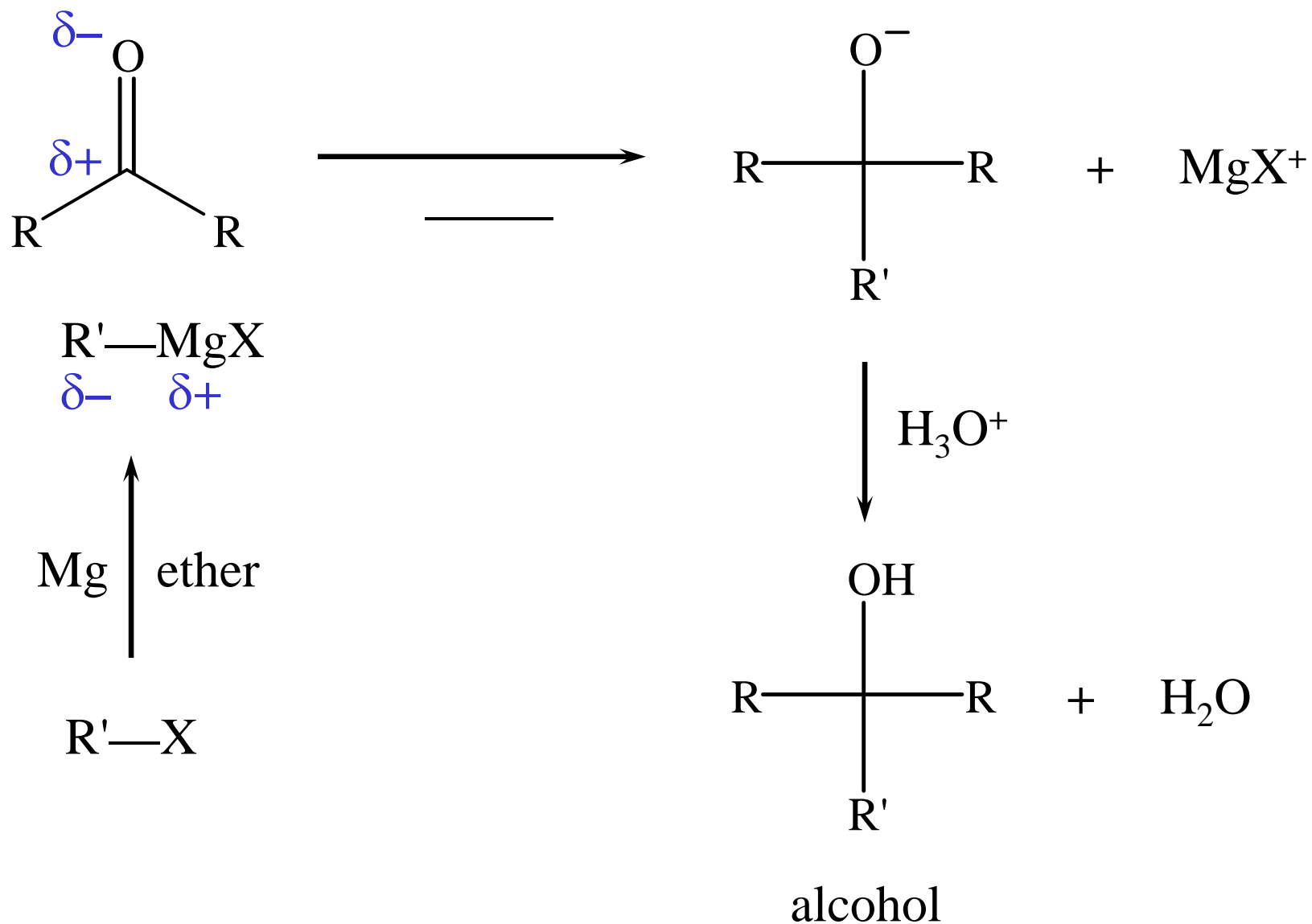
Water, H₂O
K_a = 10^{-15.7}

Carboxylic acids, RCO₂H
K_a ≈ 10⁻⁵

Amines, R₂NH
K_a ≈ 10⁻³⁸

Alcohols, ROH
K_a ≈ 10[—]

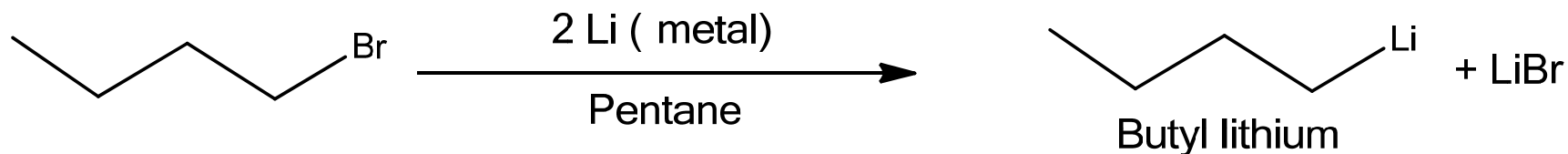
(b) Reactions with carbonyl compounds



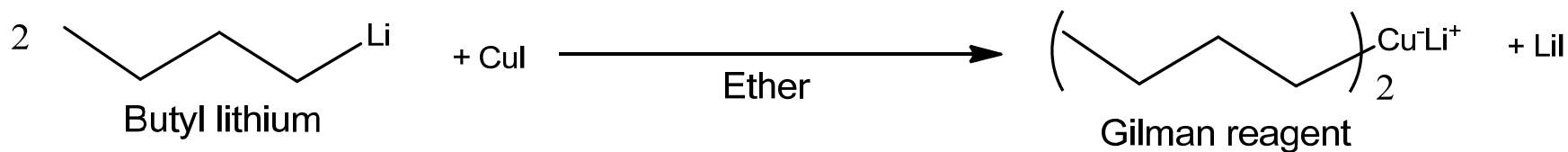
GILMAN REAGENTS: "lithium diorganocopper"

Formation is a two step process

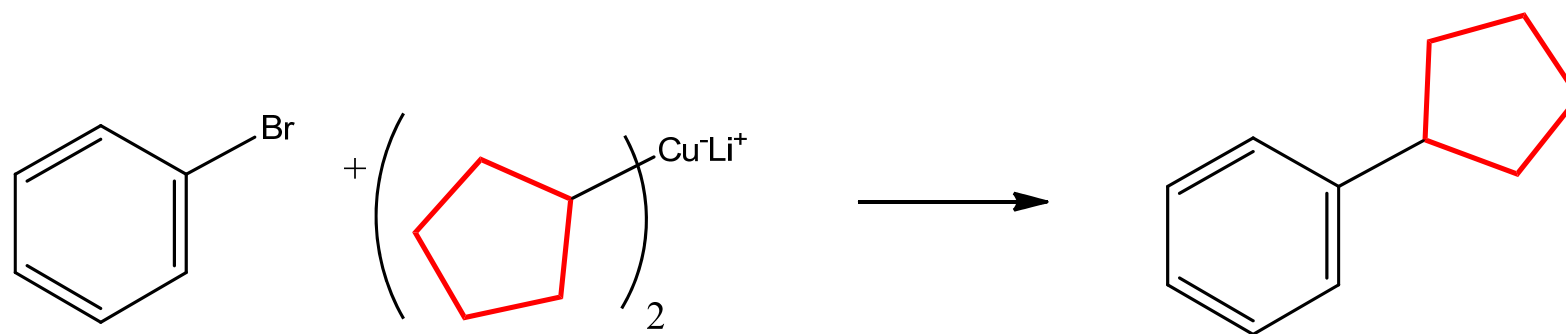
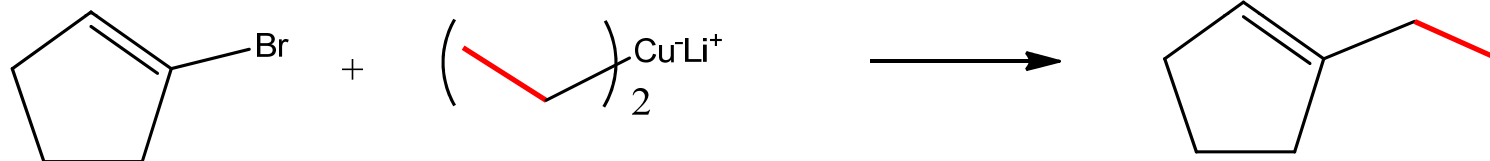
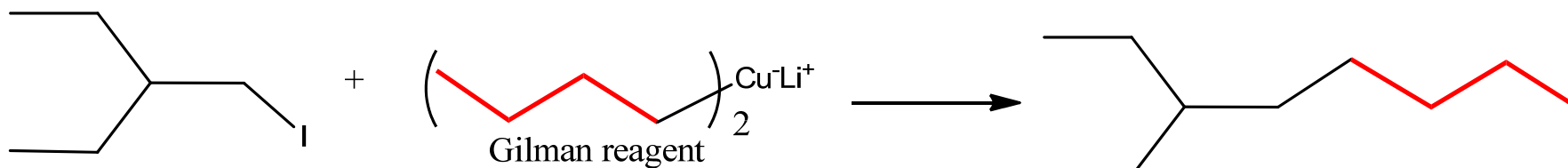
1) From alkyl halide make alkyl lithium



2) From alkyl lithium make lithium diorganocopper



Use of GILMAN REAGENTS: Coupling to R-X, X = _____



Versatile method to form _____ bonds, very useful for building up carbon skeletons

Which of the following molecules would not yield the desired organolithium reagent when treated with Li in pentane?

1. iododecane
2. 4-bromo-1-pentanol
3. phenyl bromide
4. 4-bromobutyl methyl ether
5. cyclohexylbromide

OXIDATION AND REDUCTION in ORGANIC CHEM

Oxidation

_____ electron density on carbon by:

Forming C-O, C-N, C-X (halogen)

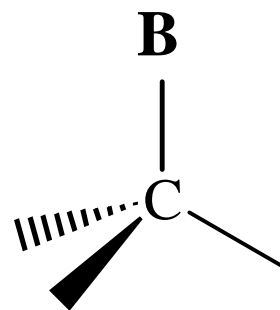
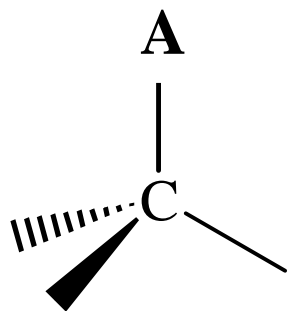
Breaking C-H

Reduction

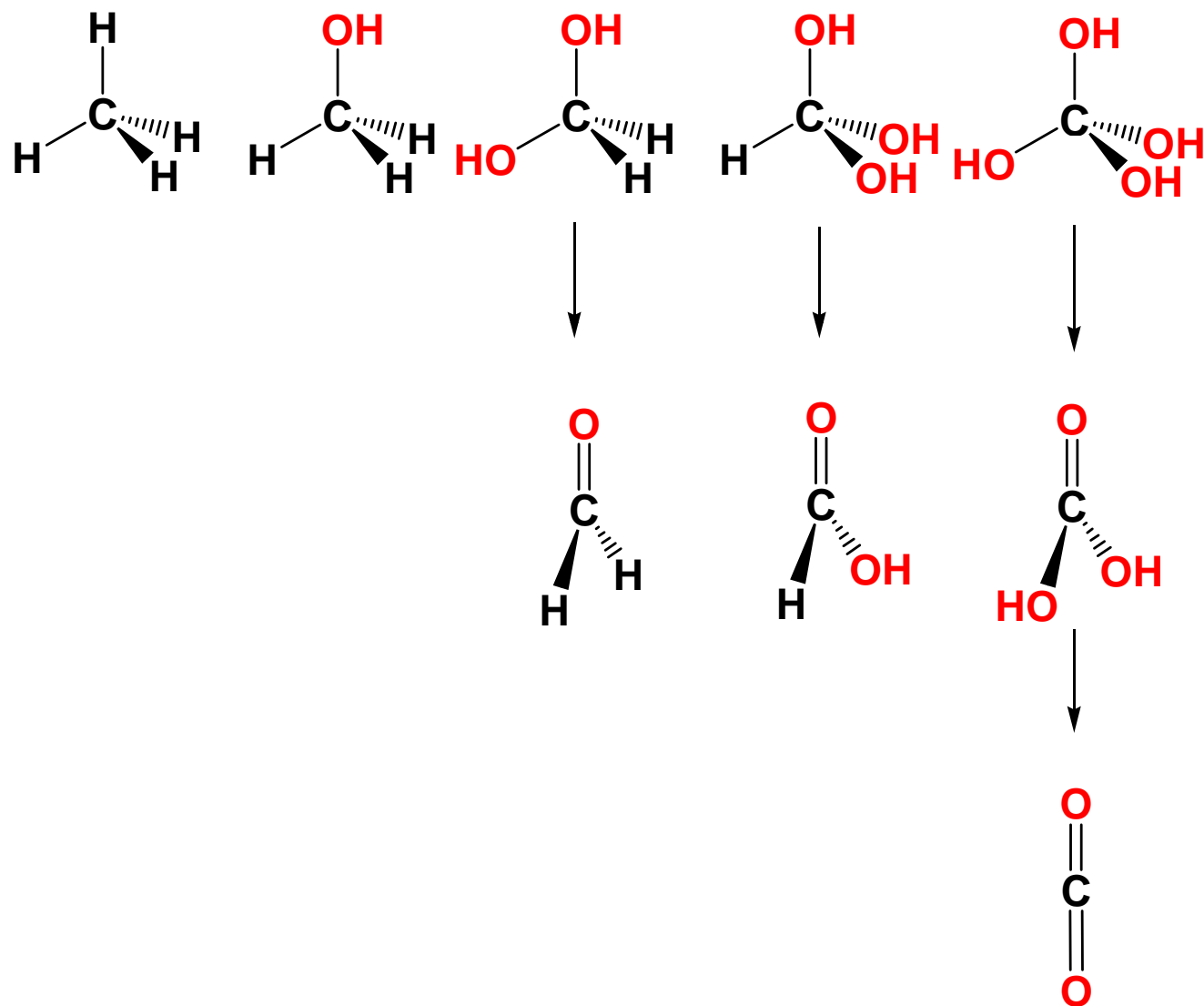
_____ electron density on carbon by:

Breaking C-O, C-N, C-X (halogen)

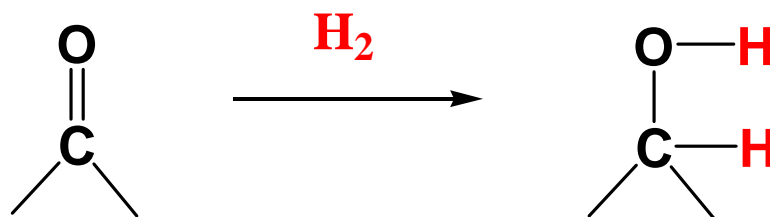
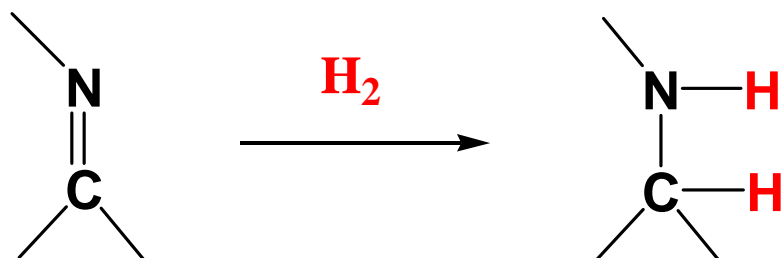
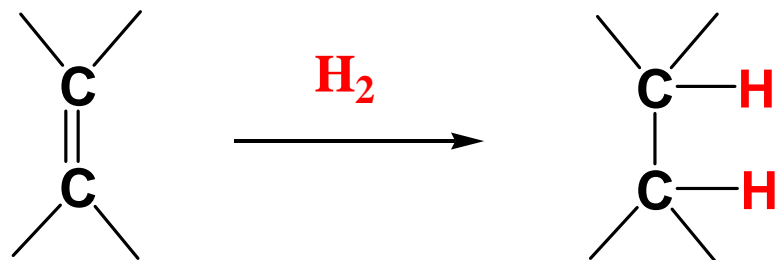
Forming C-H



LEVELS of OXIDATION



HYDROGENATION/REDUCTION



Define the following reactions as either an oxidation, reduction, or neither:

