DAMIETTA UNIVERSITY

CHEM-103:

BASIC ORGANIC CHEMISTRY

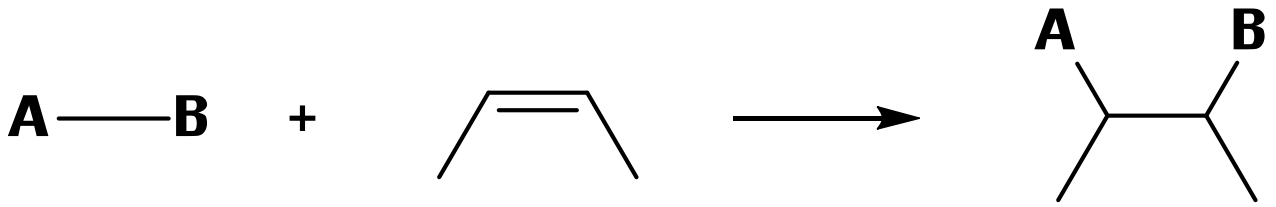
LECTURE 4

Dr Ali El-Agamey

Types of reactions

1- Addition reaction

They normally involves **unsaturated compounds** capable of accepting additional atoms.



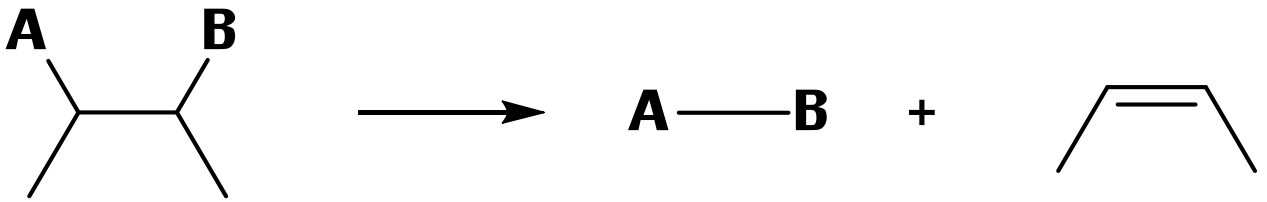
2- Substitution reaction

Atom or group **replaces** atom or group.

Types of reactions

3- Elimination reaction

Atoms are **removed** to produce unsaturated compounds or ring.

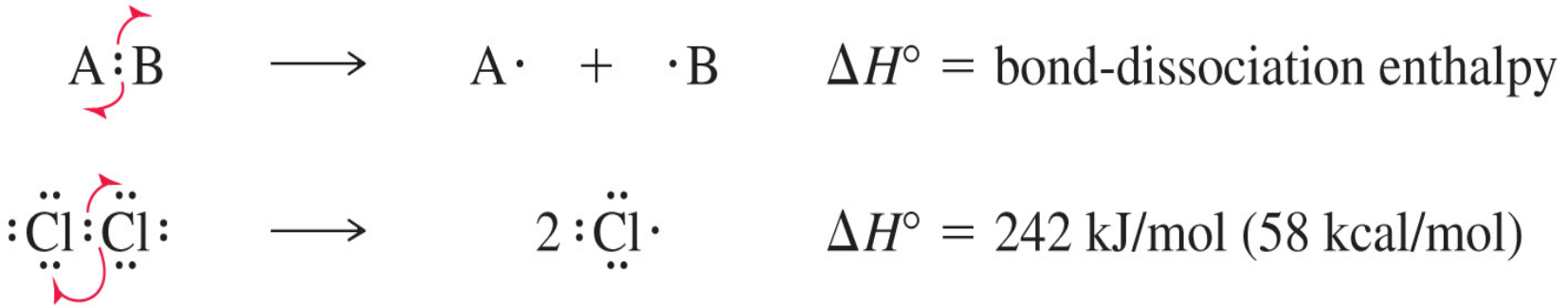


Bond-Dissociation Enthalpies (BDE)

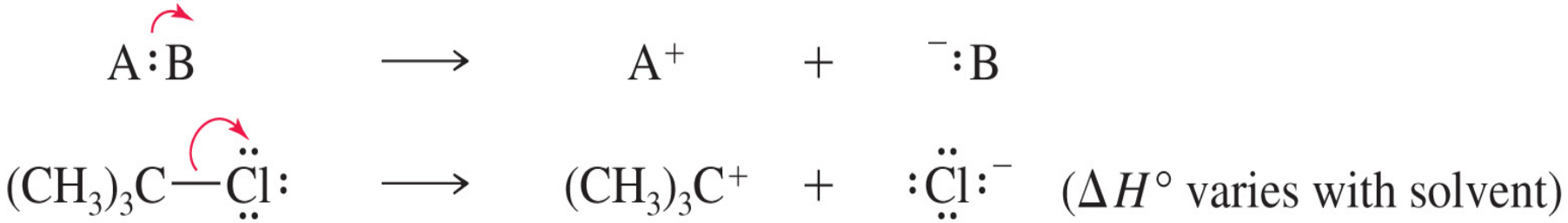
- **Bond-dissociation enthalpies** (BDE, also called Bond-dissociation energy) is the amount of enthalpy required to break a particular bond **homolytically**.
- Bond-dissociation **requires** energy (+BDE).
- Bond formation **releases** energy (-BDE).
- BDE can be used to estimate ΔH for a reaction.
    - ***Homolytic cleavage***: When the bond breaks, each atom gets one electron.
    - ***Heterolytic cleavage***: When the bond breaks, the most electronegative atom gets both electrons.

Homolytic and Heterolytic Cleavages

Homolytic cleavage (free radicals result)



Heterolytic cleavage (ions result)



Bond Dissociation Energies for the Formation of Free Radicals

Formation of a methyl radical — *Bond-dissociation enthalpy*

$\Delta H^\circ = 435$ kJ (104 kcal)

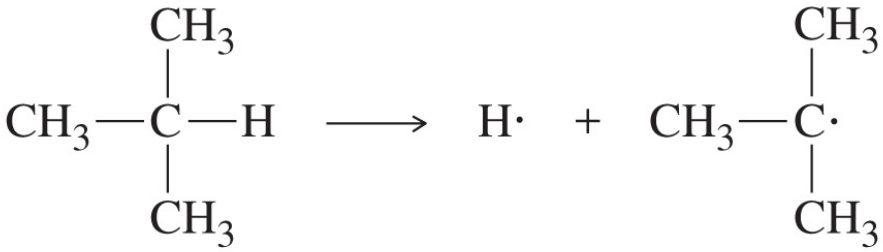
Formation of a primary (1°) radical

$\Delta H^\circ = 410$ kJ (98 kcal)

Formation of a secondary (2°) radical

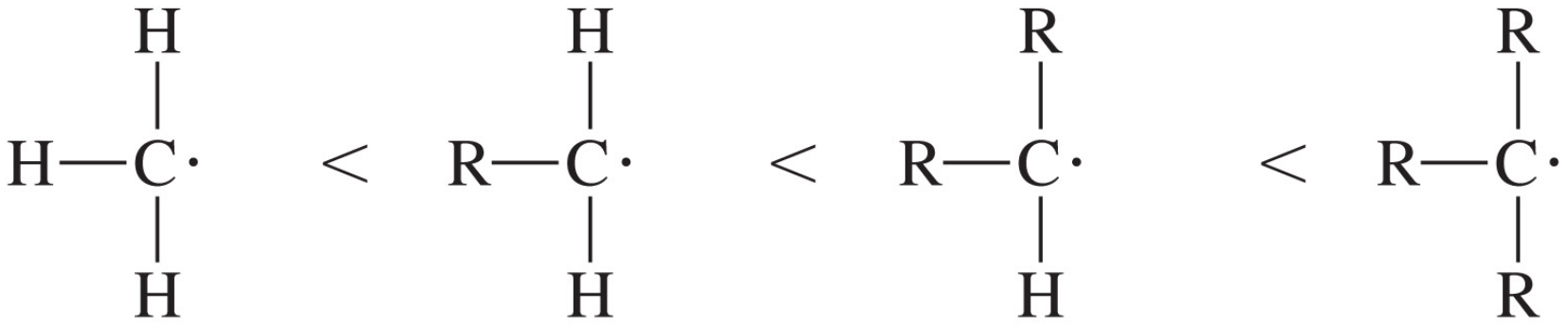
$\Delta H^\circ = 397$ kJ (95 kcal)

Formation of a tertiary (3°) radical



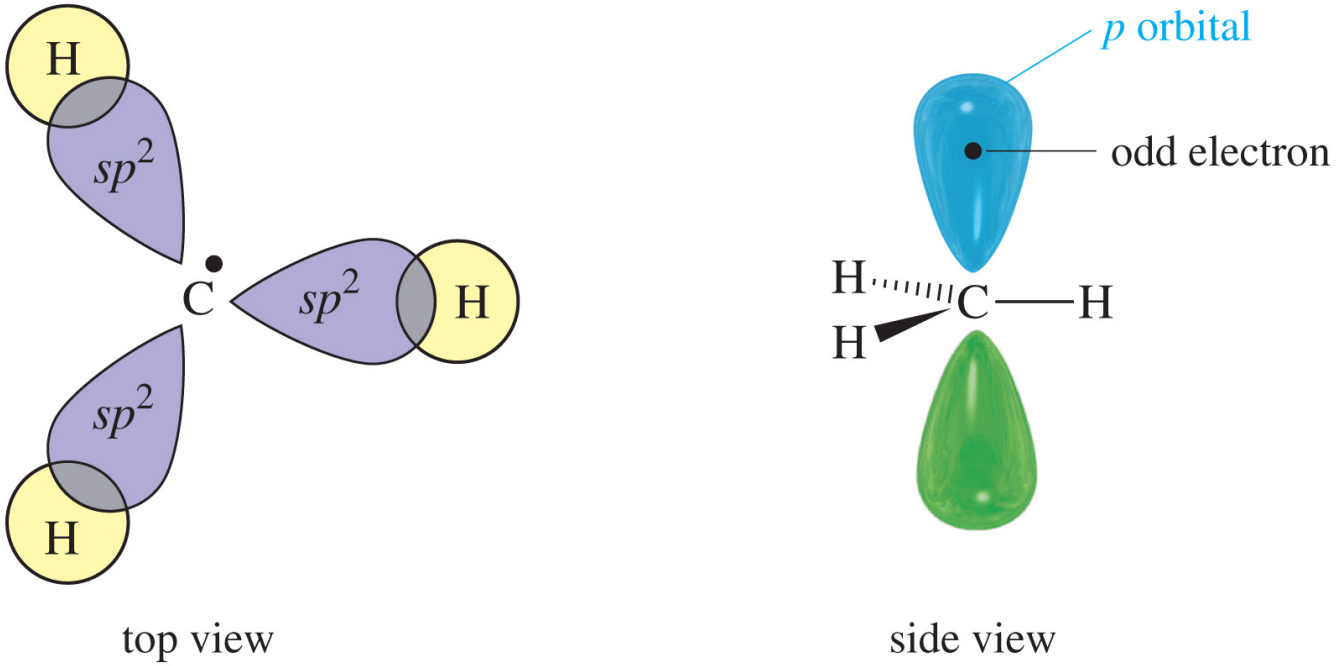
$\Delta H^\circ = 381$ kJ (91 kcal)

Stability of Free Radicals



- Free radicals are **more stable** if they are **highly substituted**.

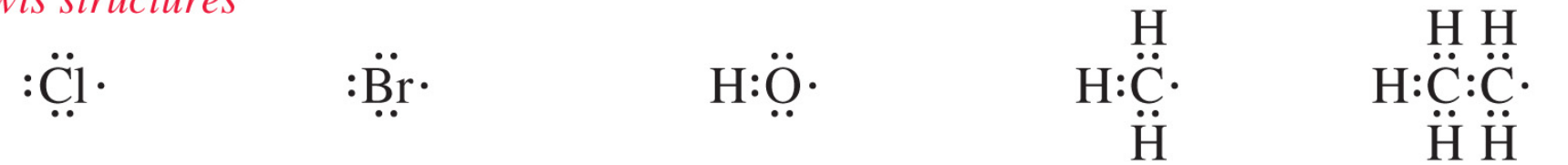
Free Radicals



- Also electron-deficient.
- Stabilized by alkyl substituents.
- Order of stability:
  3° > 2° > 1° > methyl

Lewis Structures of Free Radicals

Lewis structures



Written

$Cl\cdot$	$Br\cdot$	$HO\cdot$	$CH_3\cdot$	$CH_3CH_2\cdot$
chlorine atom	bromine atom	hydroxyl radical	methyl radical	ethyl radical

- Free radicals have **unpaired electrons**.
- Halogens have 7 valence electrons so one of them will be unpaired (radical). We refer to the halides as atoms not radicals.

Organic Chemistry, 7th Edition
L. G. Wade, Jr.

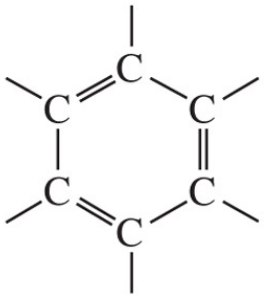
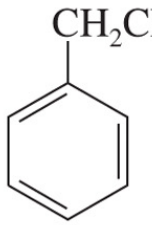
Alkanes

Hydrocarbons

Hydrocarbons are molecules that are made of **carbon and hydrogen ONLY**.

TABLE 3-1

Hydrocarbon Classifications

Compound Type	Functional Group	Example
alkanes	none (no double or triple bonds)	$CH_3—CH_2—CH_3$, propane
alkenes	$>C=C<$ double bond	$CH_2=CH—CH_3$, propene
alkynes	$—C\equiv C—$ triple bond	$H—C\equiv C—CH_3$, propyne
aromatics	benzene ring 	 ethylbenzene

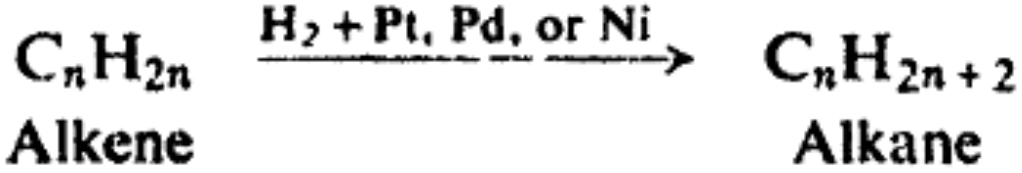
Alkanes

- General formula: C_nH_{2n+2}
- Found in everything from natural gas to petroleum.
- The smaller alkanes have very low boiling points (b.p.) therefore they are gases.

	CH_4	C_2H_6	C_3H_8
b.p.	-160°C	-89°C	-42°C

Preparation of Alkanes

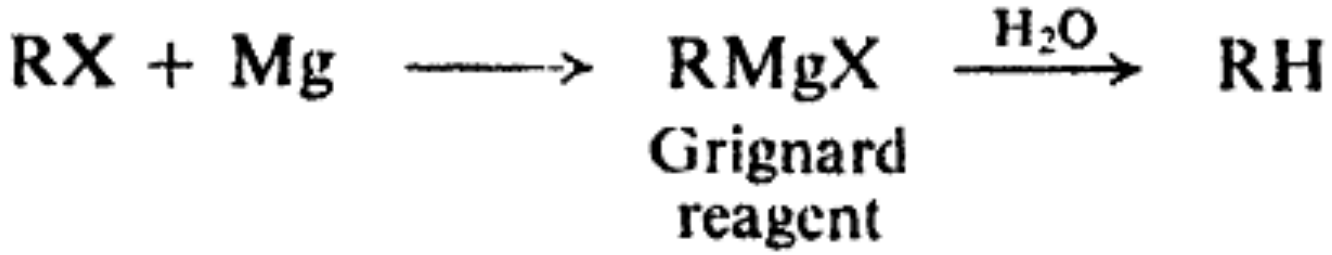
- 1- Hydrogenation of alkenes

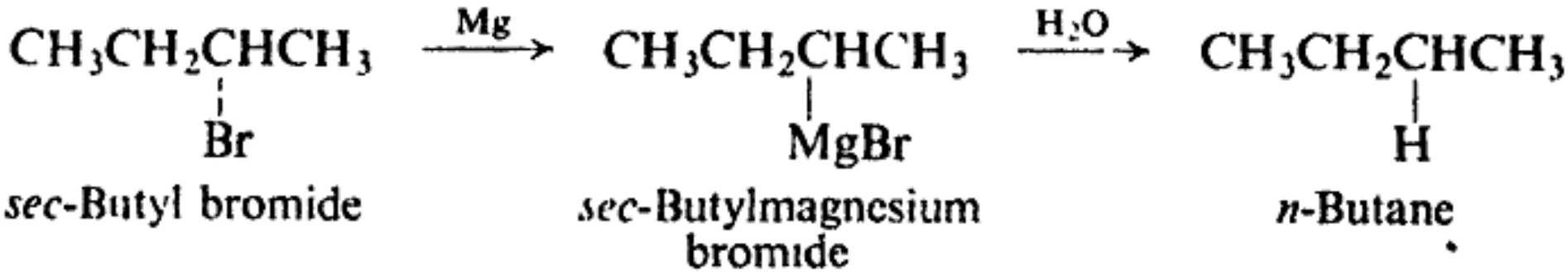


- 2- Alkyl halides
  - (a) Via hydrolysis of Grignard reagent
  - (b) Reduction by metal and acid
  - (c) Coupling with organo-copper compounds.

Preparation of Alkanes

- (a) Hydrolysis of Grignard reagent

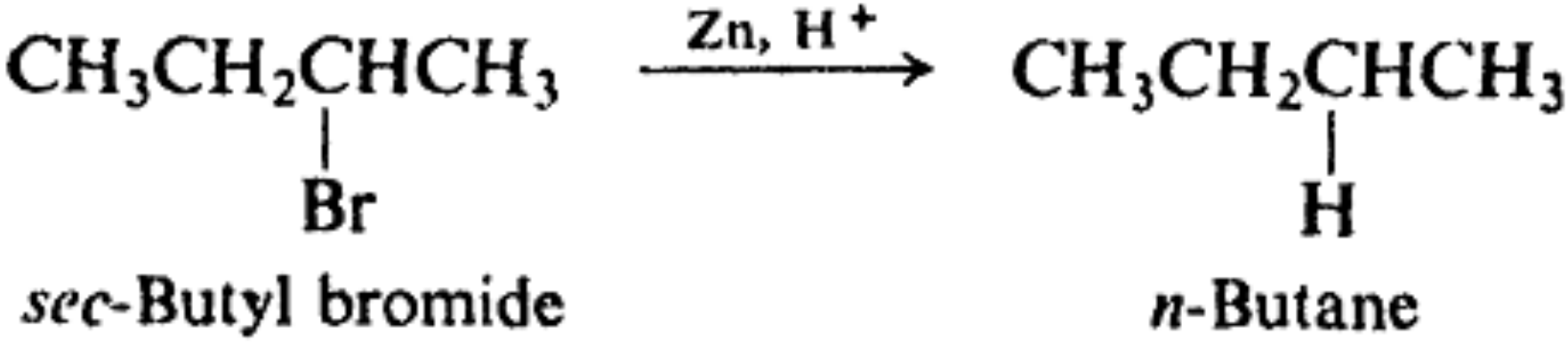




Preparation of Alkanes

- (b) Reduction by metal and acid

$$RX + Zn + H^+ \longrightarrow RH + Zn^{++} + X^-$$

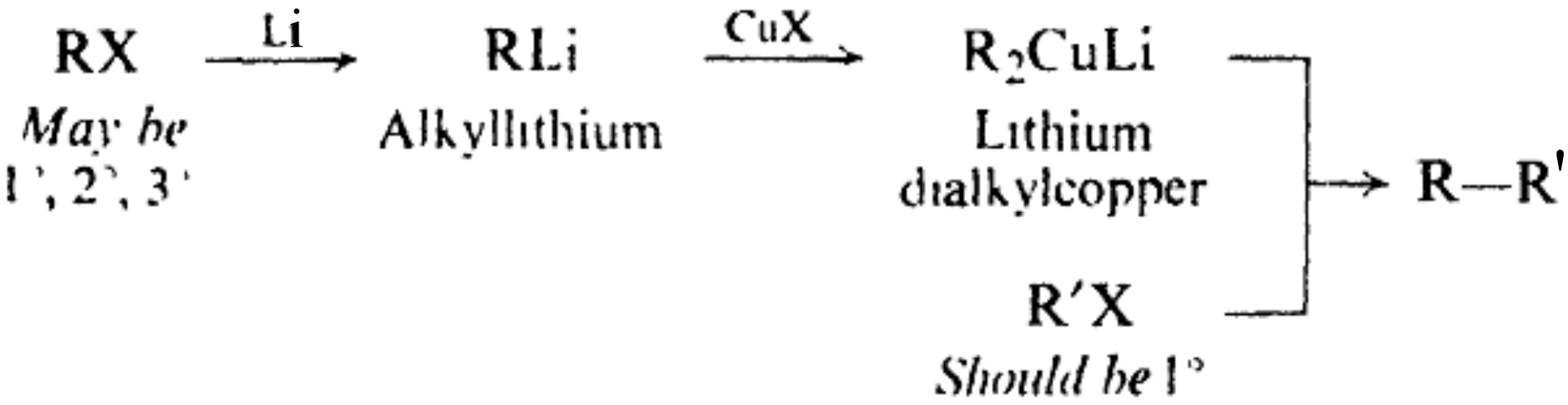


sec-Butyl bromide

n-Butane

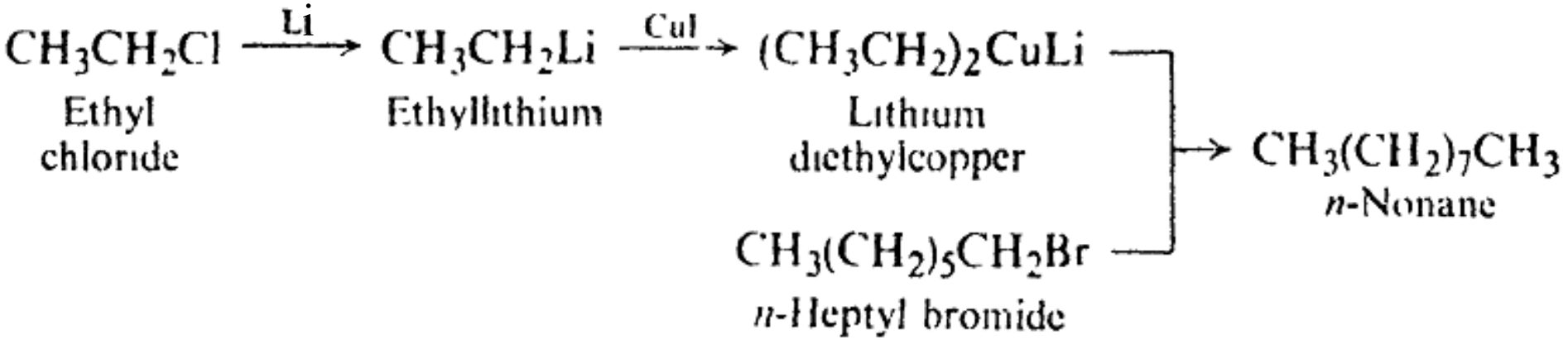
Preparation of Alkanes

- (c) Coupling with organo-copper compounds.



Preparation of Alkanes

- (c) Coupling with organo-copper compounds.



Homework

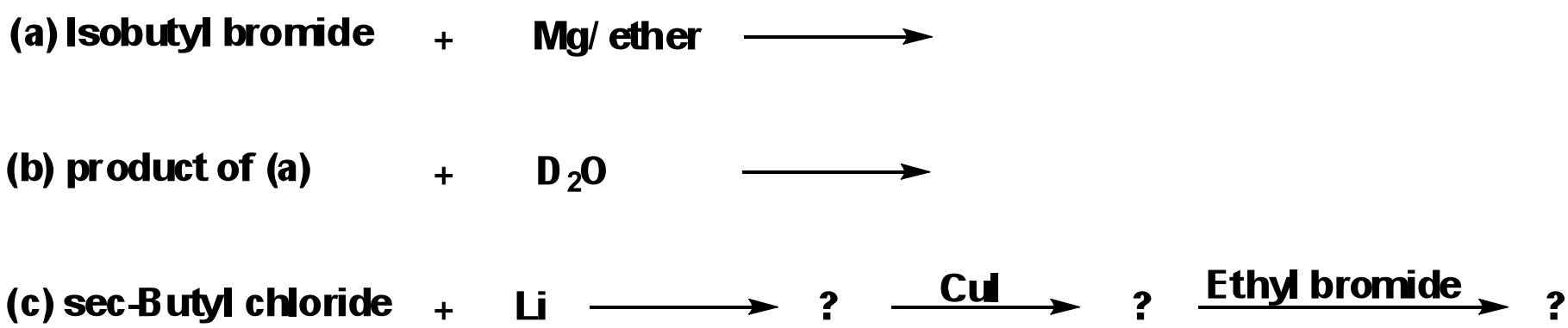
(1) Show how can you prepare **n-butane** from:[1]

(a) n-butyl bromide

(b) sec-butyl bromide and

(c) 2-butene.

Complete the following equations:[1]



Reactions of Alkanes

- **1- Combustion**

- **2- Cracking (Pyrolysis)**

- **3- Halogenation**
  - General reaction; examples
  - General mechanism; mechanism of specific example (CH_4; propane)
  - Calculation of relative reactivities; Product ratios

Reactions of Alkanes

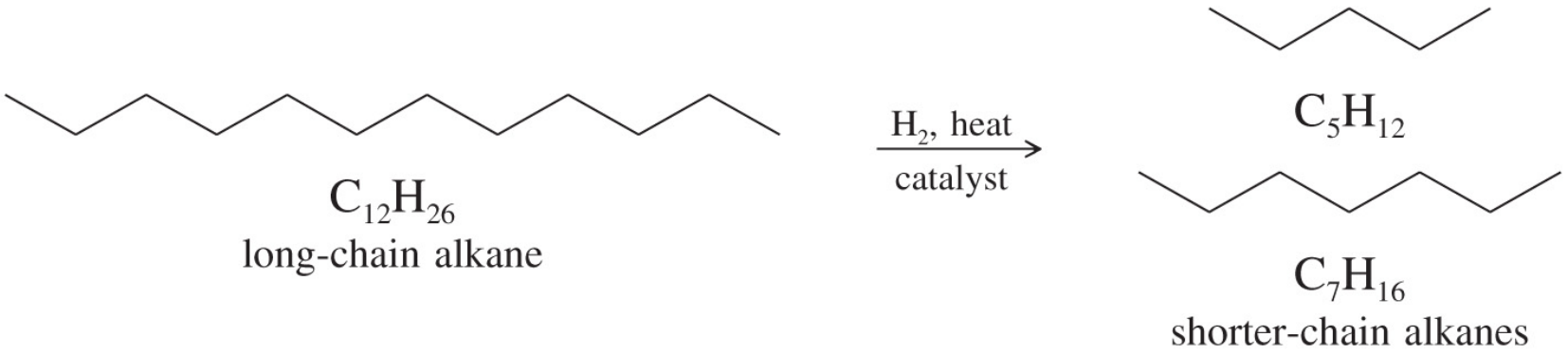
- **1- Combustion**

$$C_nH_{2n+2} + \text{Excess } O_2 \xrightarrow{\text{Flame}} n\,CO_2 + (n+1)\,H_2O \qquad \Delta H = \text{Heat of combustion}$$

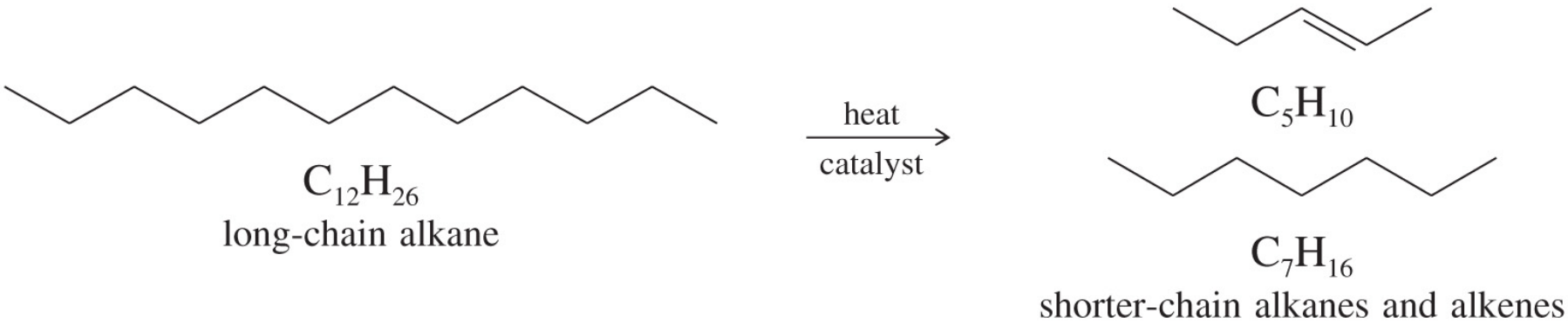
$$C_5H_{12} + 8\,O_2 \xrightarrow{\text{Flame}} 5\,CO_2 + 6\,H_2O \qquad \Delta H = -845\ \text{kcal/mol}$$

2-Cracking (Pyrolysis)

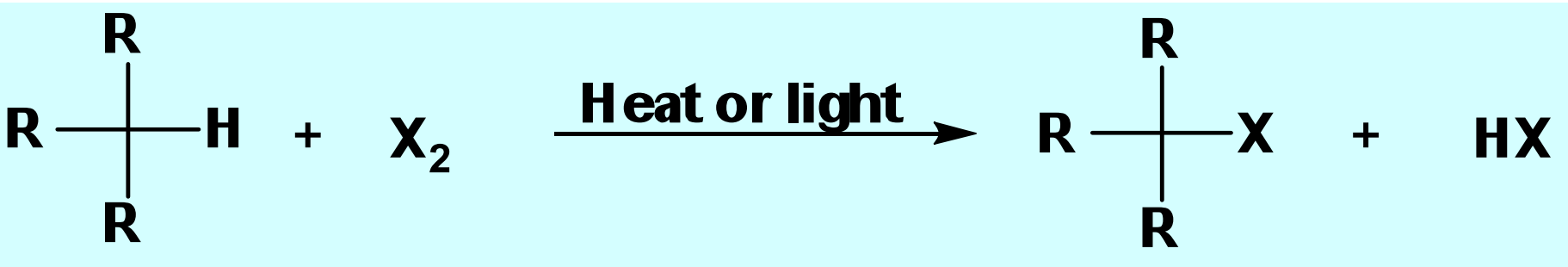
Catalytic hydrocracking



Catalytic cracking



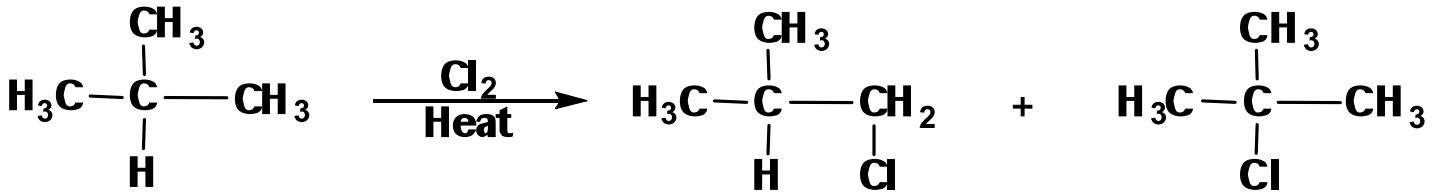
(3) Halogenation

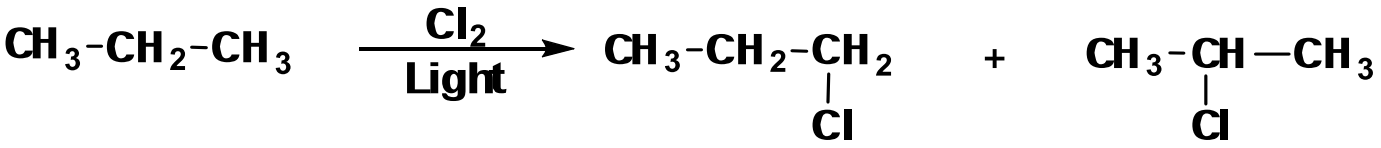


Reactivity X_2: Cl_2 > Br_2

H: 3° > 2° > 1° > CH_3-H

Examples





Homework

- **4.40 Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical chlorination yields**

  (a) A single monochloride

  (b) Four isomeric monochlorides

  (c) Three isomeric monochlorides

  (d) Two isomeric dichlorides