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Organic Chemistry

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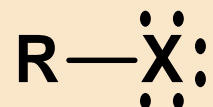
Alkyl Halides

Chapter 7

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7 Structure

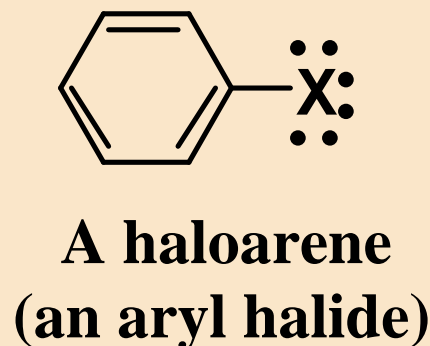
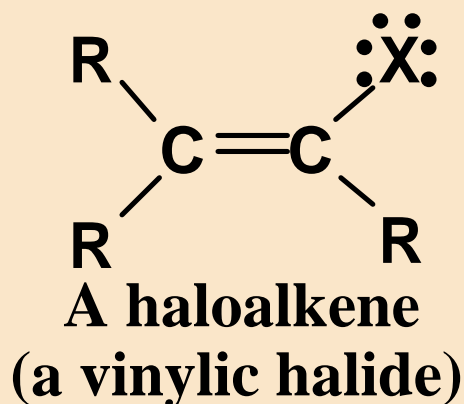
- u **Alkyl halide:** a compound containing a halogen atom covalently bonded to an sp^3 hybridized carbon atom
 - given the symbol RX



A haloalkane
(an alkyl halide)

7 Vinylic and Aryl Halides

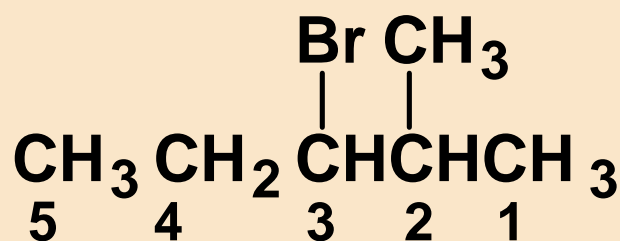
- u If the halogen is bonded to an sp^2 hybridized carbon, it is called a **vinylic halide**
- u If it is bonded to a benzene ring, it is called an **aryl halide**, given the symbol Ar-X



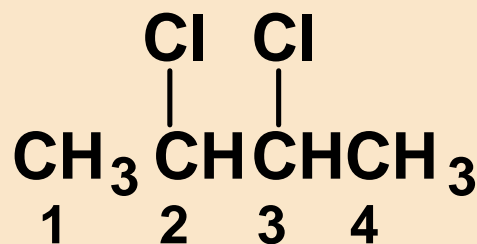
- we do not study vinylic and aryl halides in this chapter

7 Nomenclature

- locate the parent alkane
- number the parent chain to give the substituent encountered first, be it halogen or an alkyl group, the lower number
- halogen substituents are indicated by the prefixes fluoro-, chloro-, bromo-, and iodo- and listed in alphabetical order with other substituents



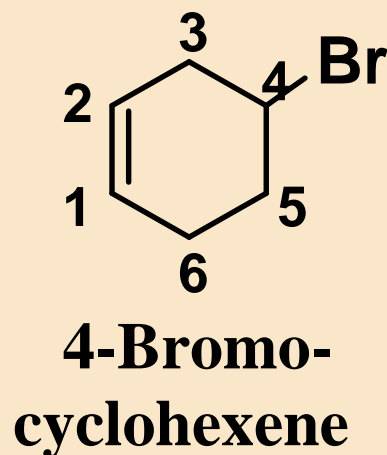
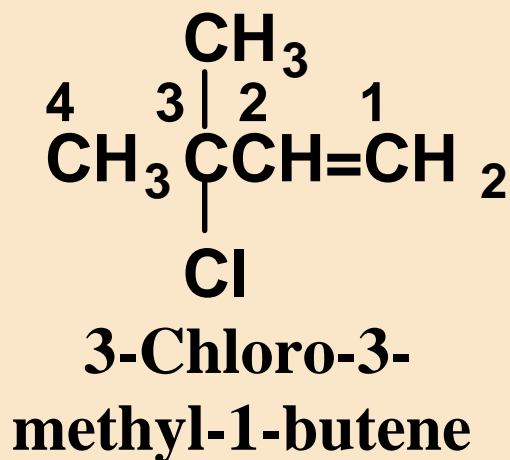
3-Bromo-2-methylpentane



2,3-Dichlorobutane

7 Nomenclature

- u For haloalkenes, numbering is determined by the location of the C-C double bond

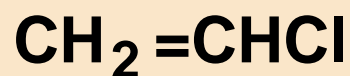


7 Nomenclature

- u Common names - name the alkyl group followed by the name of the halide



Chloroethane
(Ethyl chloride)



Chloroethene
(Vinyl chloride)



3-Chloropropene
(Allyl chloride)

7 Nomenclature

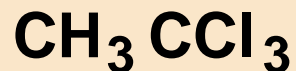
- u Several polyhaloalkanes are common solvents and are generally referred to by their common or trivial names



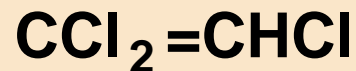
Dichloromethane
(Methylene chloride)



Trichloromethane
(Chloroform)



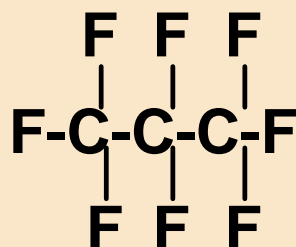
1,1,1-Trichloroethane
(Methyl chloroform)



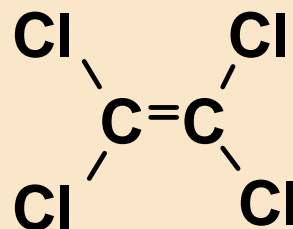
Trichloroethylene
(Trichlor)

7 Nomenclature

- u Hydrocarbons in which all hydrogens are replaced by halogens are commonly named as perhaloalkanes or perhaloalkenes



Perfluoropropane



Perchloroethylene

7 Dipole Moments

u Dipole moment of RX depends on:

- the sizes of the partial charges,
- the distance between them, and
- the polarizability of the unshared electrons on halogen

	Electronegativity of X	C-H Bond Length (Å)	Dipole Moment (D)
CH ₃ F	4.0	1.39	1.85
CH ₃ Cl	3.0	1.78	1.87
CH ₃ Br	2.8	1.93	1.81
CH ₃ I	2.5	2.14	1.62

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7 van der Waals forces

- u **van der Waals forces - a group of intermolecular forces, including**
 - **dipole-dipole**
 - **dipole-induced dipole**
 - **induced dipole - induced dipole (dispersion forces)**

- u **As atoms or molecules are brought closer together, van der Waals attractive forces are overcome by repulsive forces between electron clouds of adjacent atoms**

7 van der Waals radii

- u Energy minimum is where net attractive forces are the strongest
- u Nonbonded interatomic and intermolecular distances at these minima can be measured by x-ray crystallography
- u Each atom or group of atoms can be assigned an atomic or molecular radius called a van der Waals radius

7 van der Waals radii

H	F	Cl	Br	CH ₂	CH ₃	I
1.2	1.35	1.80	1.95	2.0	2.0	2.15

Increasing van der Waals radius (Å) 

u Notice that

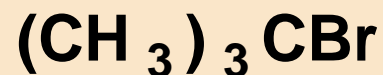
- F is only slightly larger than H
- among the halogens, only I is larger than CH₃

7 Boiling Points

- u Among constitutional isomers, branched isomers
 - have a more compact shape,
 - decreased area of contact and decreased van der Waals attractive forces between neighbors,
 - and lower boiling points



bp 100°C

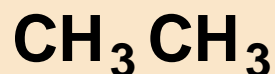


bp 72°C

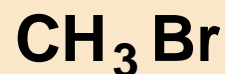
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7 Boiling Points

- u For an alkane and an alkyl halide of comparable size and shape, the alkyl halide has the higher boiling point
 - the difference is due almost entirely to the greater polarizability of the three unshared pairs of electrons on halogen compared with the polarizability of shared electron pairs of the hydrocarbon



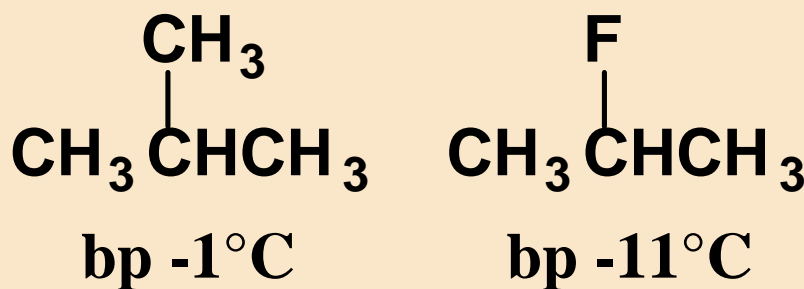
bp -89°C



bp 4°C

7 Boiling Points

- u Boiling points of alkyl fluorides are lower than those of hydrocarbons of comparable molecular weight
 - the difference is due to the small size of fluorine, the tightness with which its electrons are held, and their particularly low polarizability



7 Density

- u The densities of liquid alkyl halides are greater than those of hydrocarbons of comparable molecular weight**
 - a halogen has a greater mass per volume than a methyl or methylene group**
- u Some liquid alkyl chlorides are less dense than water**
- u All liquid alkyl bromides and iodides are more dense than water**

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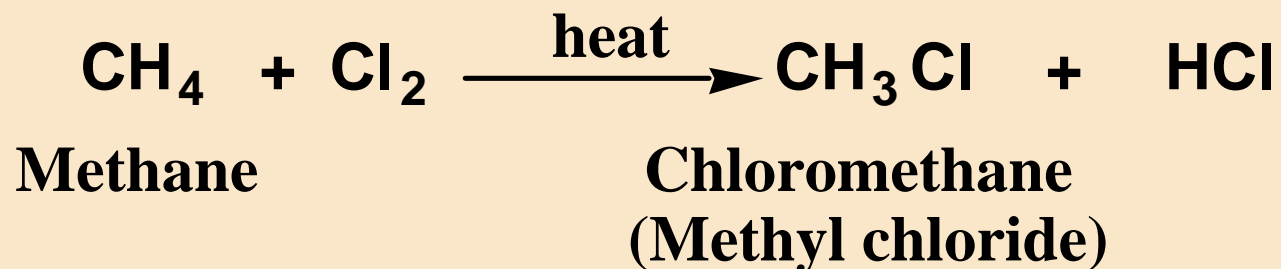
7 Bond Lengths, Strengths

- u C-F bonds are stronger than C-H bonds; C-Cl, C-Br, and C-I bonds are weaker

Bond	Bond Length (Å)	BDE (kcal/mol)
C—H	1.09	90-100
C—F	1.42	105
C—Cl	1.78	80
C—Br	1.93	65
C—I	2.14	50

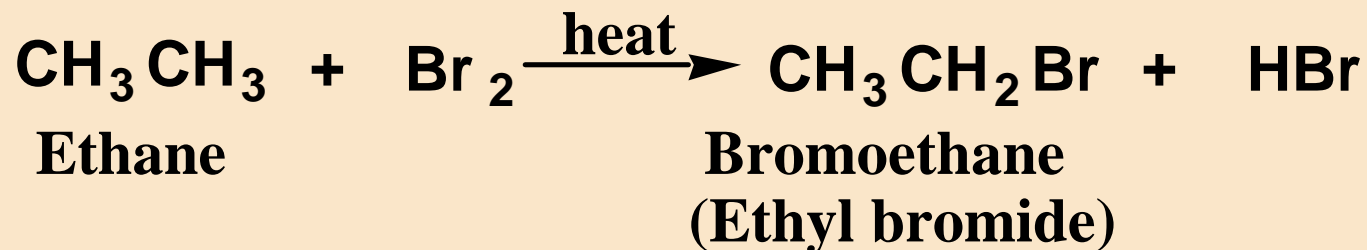
7 Halogenation of Alkanes

- u If a mixture of methane and chlorine is kept in the dark at room temperature, no change occurs
- u If the mixture is heated, or exposed to visible or ultraviolet light, reaction begins at once with the evolution of heat



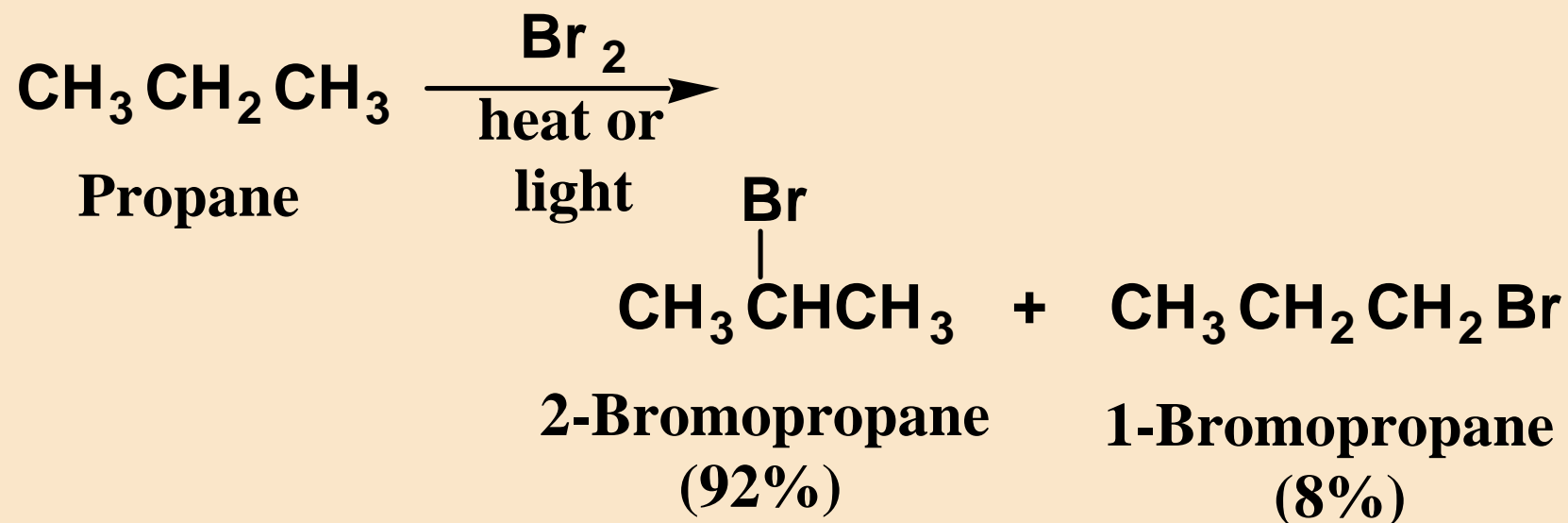
7 Halogenation of Alkanes

- u What occurs is a substitution reaction, in this case, substitution of a chlorine atom for a hydrogen atom in methane
- u **Substitution:** a reaction in which an atom or group of atoms is replaced by another atom or group of atoms



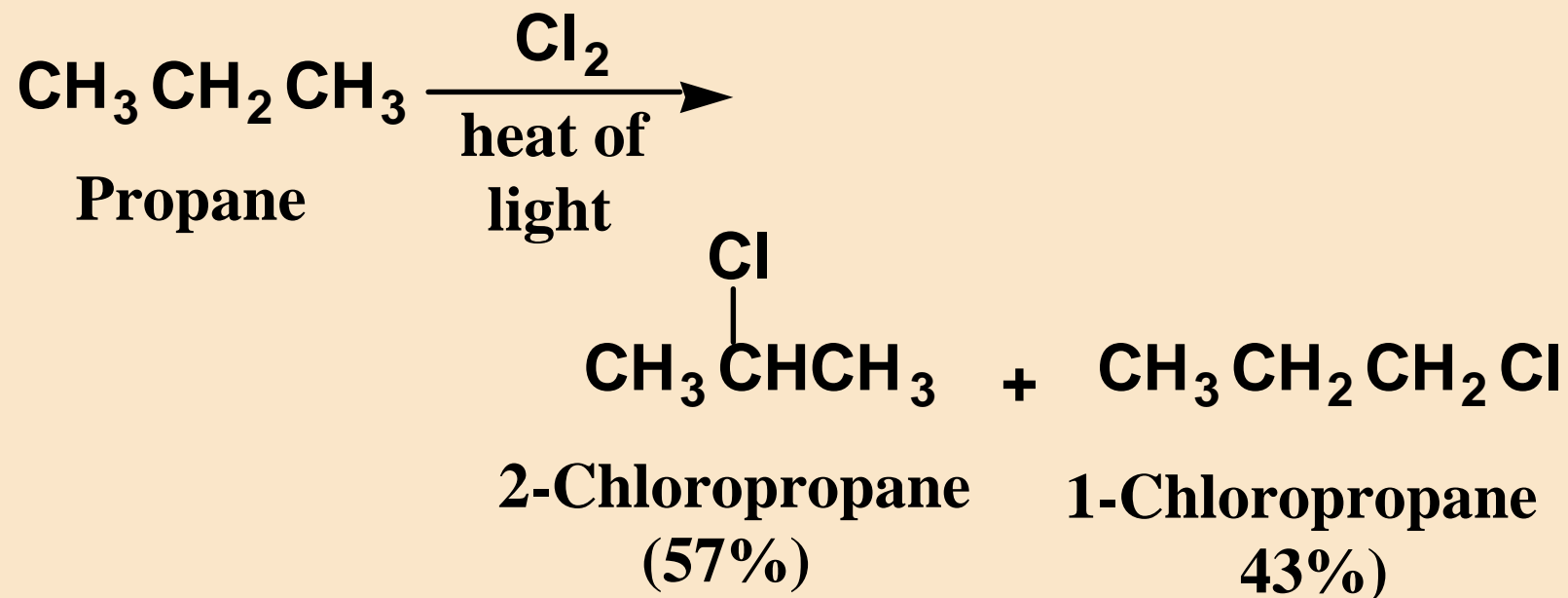
7 Regioselectivity

- u Regioselectivity of 2° hydrogen over a 1° hydrogen is high for bromination



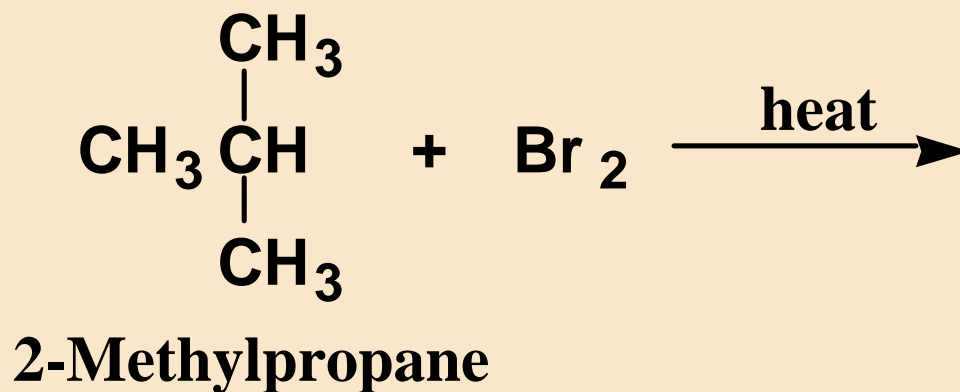
7 Regioselectivity

u but not as high for chlorination



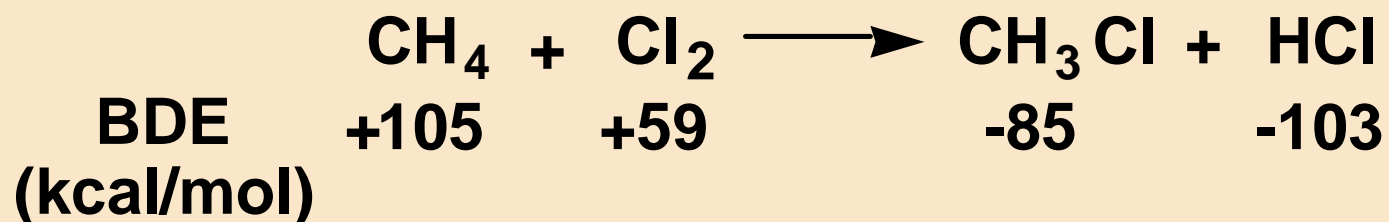
7 Regioselectivity

- u Regioselectivity is $3^\circ > 2^\circ > 1^\circ$
 - for bromination - approximately 1600:80:1
 - for chlorination - approximately 5:4:1
- u **Example:** draw all monobromination products and predict the % of each for this reaction



7 Energetics

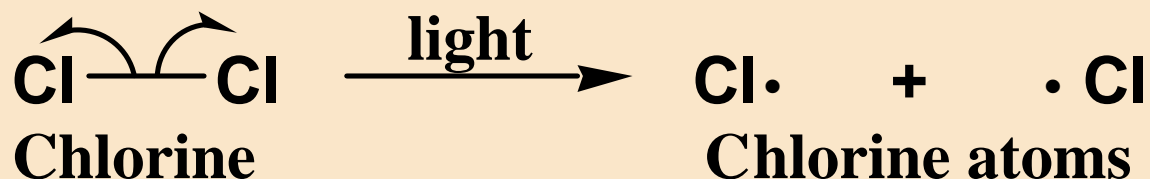
- u Using BDE (Appendix 3), we can calculate the heat of reaction, ΔH° , for the halogenation of an alkane



$$\Delta H^\circ = +105 + 59 + (-85) + (-103) = -24 \text{ kcal/mol}$$

7 Mechanism

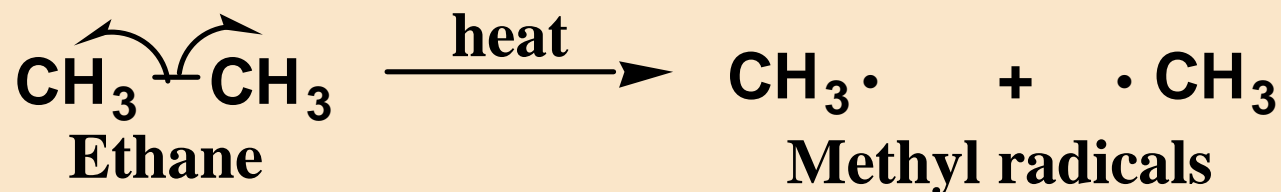
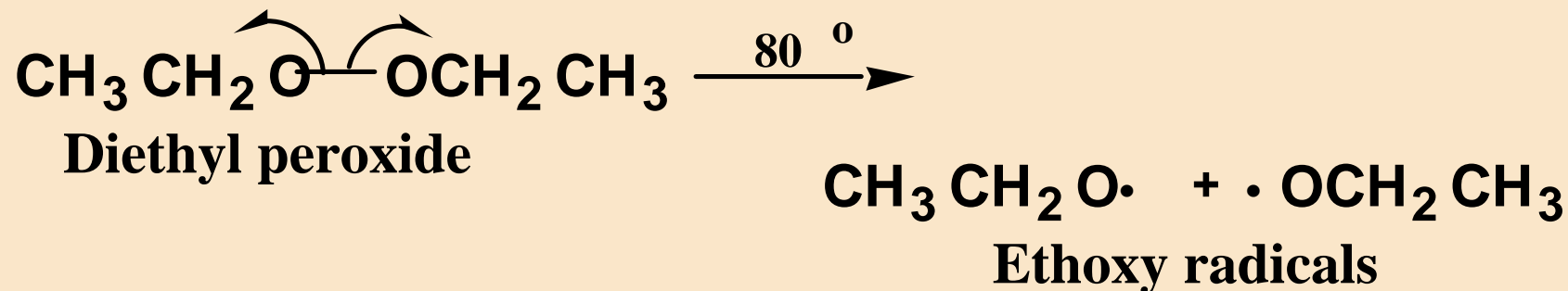
- u A radical chain mechanism
- u **Radical:** any chemical species that contains one or more unpaired electrons
- u Radicals are formed by homolytic cleavage of a bond



- a barbed curved (fishhook) arrow is used to show the change in position of a single electron

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7 Formation of Radicals



u The order of stability of alkyl radicals is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$

7 Mechanism

- u **Chain initiation:** a step in a radical chain reaction characterized by formation of radicals from nonradical compounds

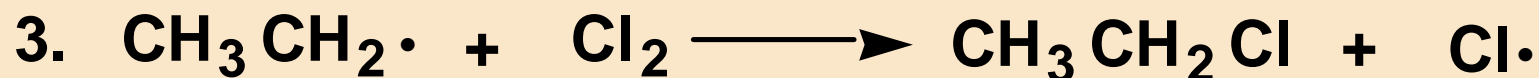
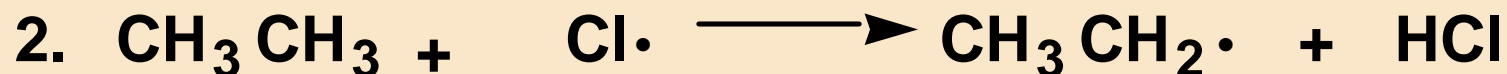
Chain initiation



7 Mechanism

- u **Chain propagation:** a step in a radical chain reaction characterized by reaction of a radical and a molecule to form a new radical

Chain propagation

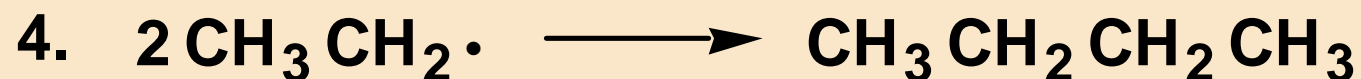


- u **Chain length, n:** the number of times the cycle of chain propagation steps repeats in a chain reaction

7 Mechanism

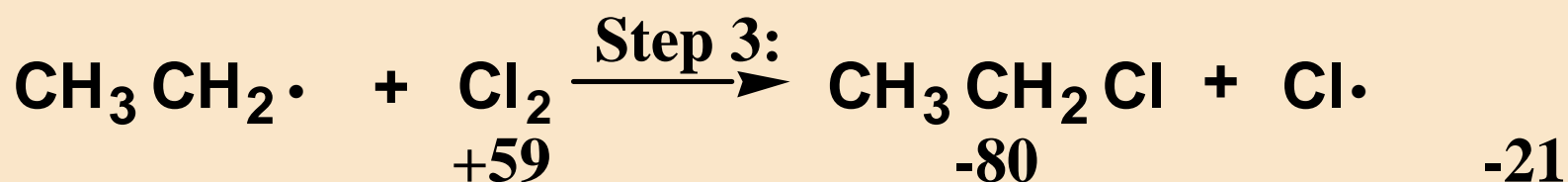
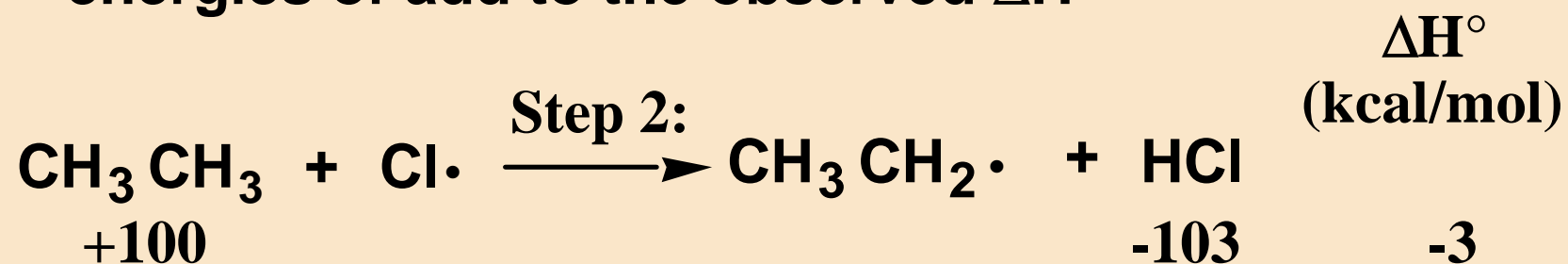
- u **Chain termination** - a step in a radical chain reaction that involves destruction of radicals

Chain termination



7 Chain Propagation Steps

- u For any set of chain propagation steps, their
- equations add to the observed stoichiometry
 - energies of add to the observed ΔH°



7 Regioselectivity?

- u The regioselectivity of chlorination and bromination can be accounted for in terms of the relative stabilities of alkyl radicals ($3^\circ > 2^\circ > 1^\circ >$ methyl)
- u But how do we account for the greater regioselectivity of bromination (1600:80:1) compared with chlorination (5:4:1)?

7 Hammond's Postulate

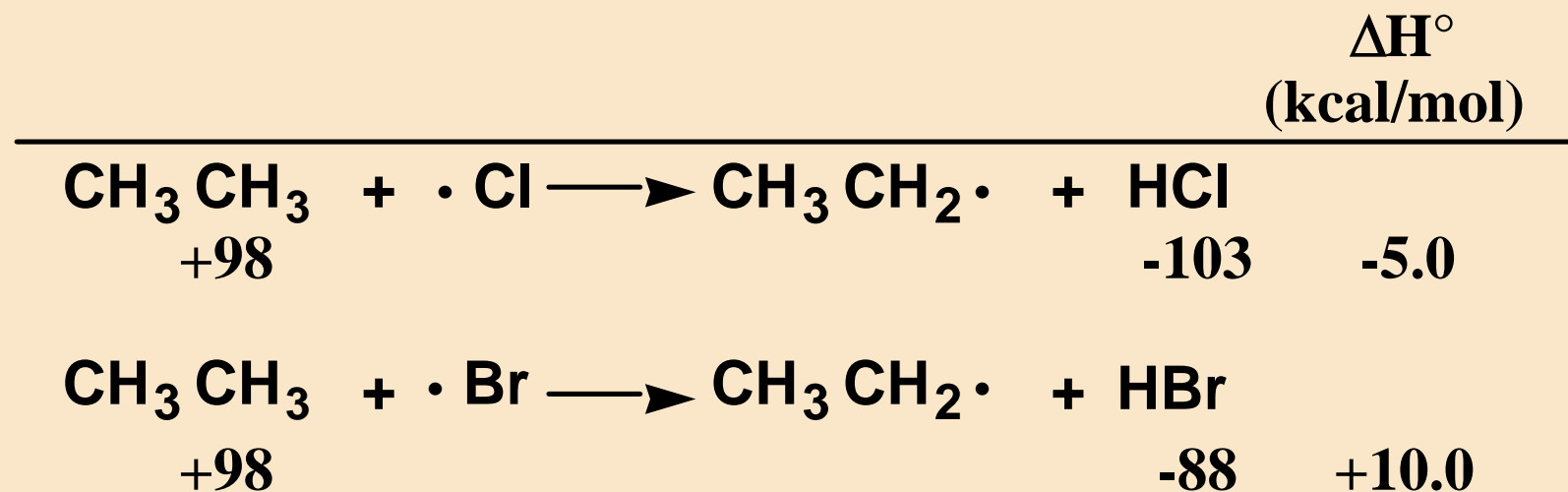
u **Hammond's Postulate:** the structure of the transition state

- for an exothermic reaction looks more like the reactants of that step
- for an endothermic reaction looks more like the products of that step

u This postulate applies equally well to the transition state for a one-step reaction and to each transition state in a multi-step reaction

7 Hammond's Postulate

- u In halogenation of an alkane, the rate-limiting step is hydrogen abstraction
 - this step is exothermic for chlorination and endothermic for bromination



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7 Hammond's Postulate

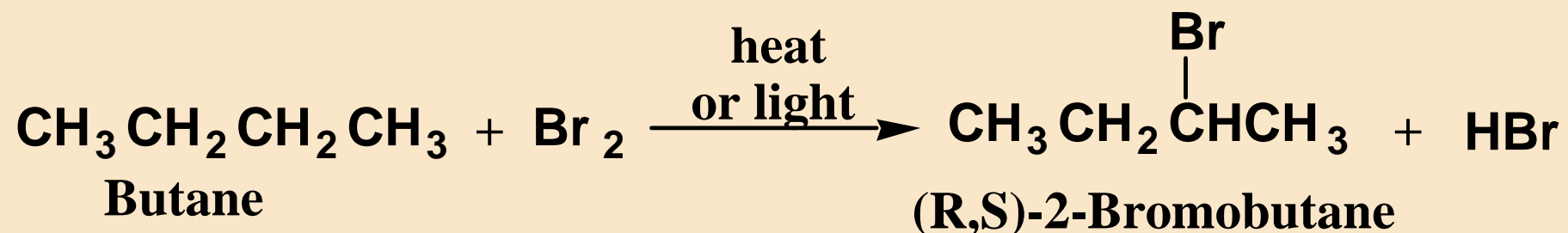
- u **Because hydrogen abstraction for chlorination is exothermic,**
 - **the transition state resembles the alkane and a chlorine atom,**
 - **there is little radical character on carbon in the transition state, and**
 - **regioselectivity is only slightly influenced by radical stability**

7 Hammond's Postulate

- u Because hydrogen abstraction for bromination is endothermic,
 - the transition state resembles an alkyl radical and HBr,
 - there is significant radical character on carbon in the transition state, and
 - regioselectivity is greatly influenced by radical stability.
 - Radical stability is $3^\circ > 2^\circ > 1^\circ > \text{methyl}$, and regioselectivity is in the same order

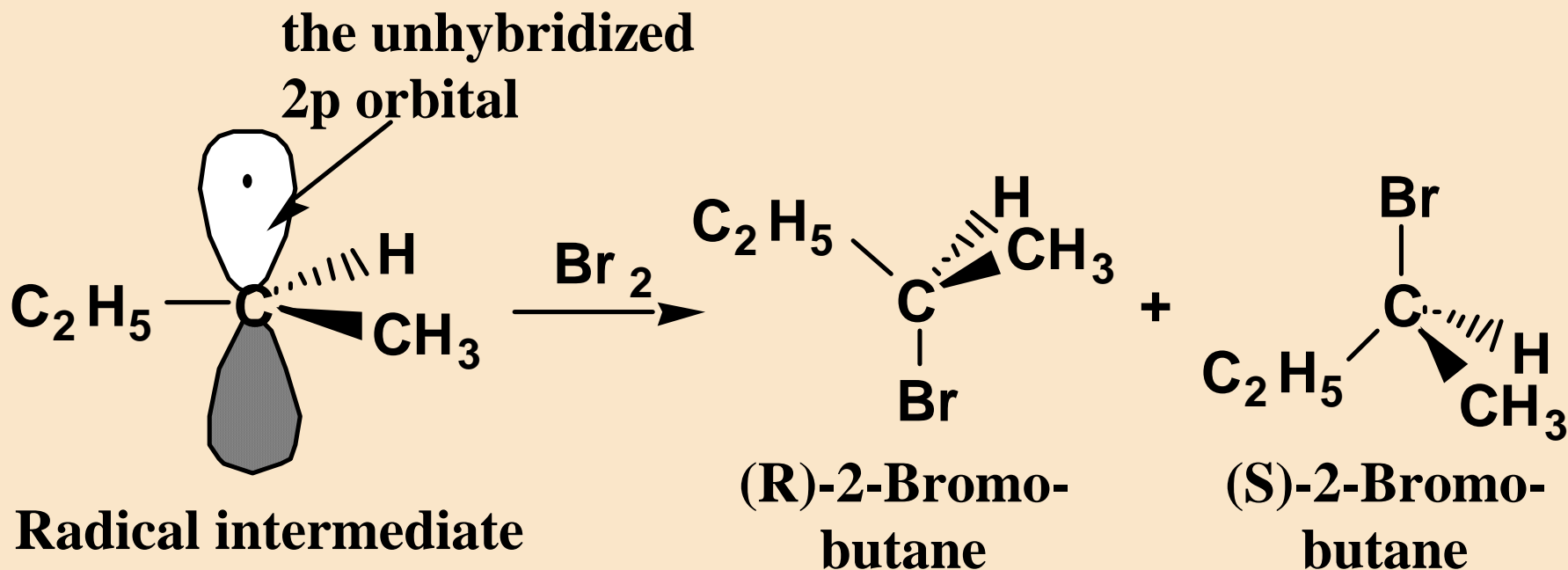
7 Stereochemistry

- u When radical halogenation produces a stereocenter or takes place at a hydrogen on an existing stereocenter, the product is an R,S mixture



7 Stereochemistry

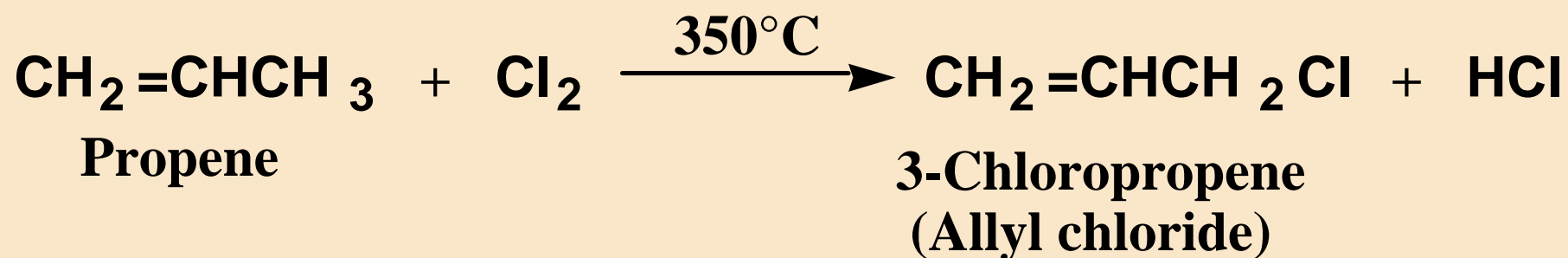
- u For simple alkyl radicals, the carbon bearing the radical is sp^2 hybridized and the unpaired electron occupies the unhybridized 2p orbital



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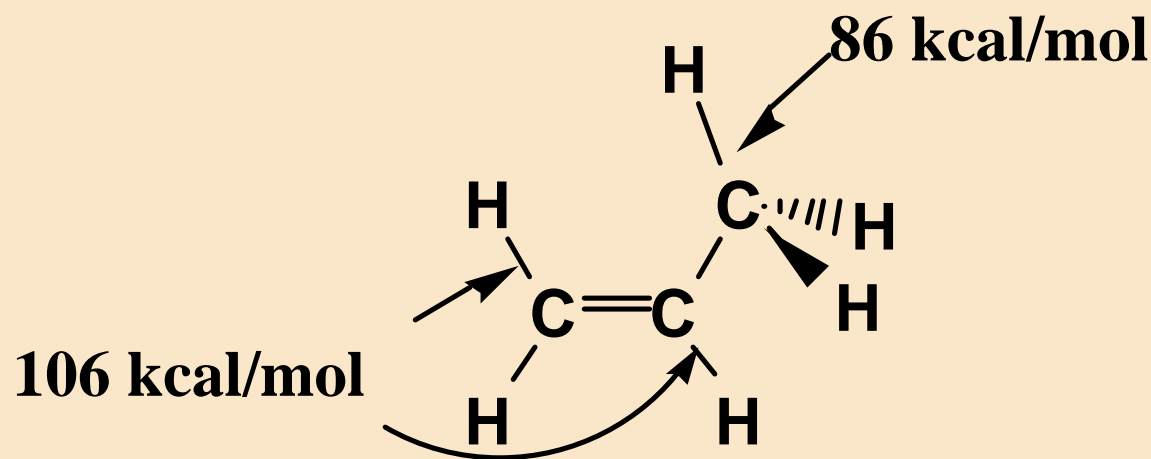
7 Allylic Halogenation

- u **Allylic carbon:** a carbon adjacent to a C-C double bond
- u **Allylic hydrogen:** a hydrogen on an allylic carbon



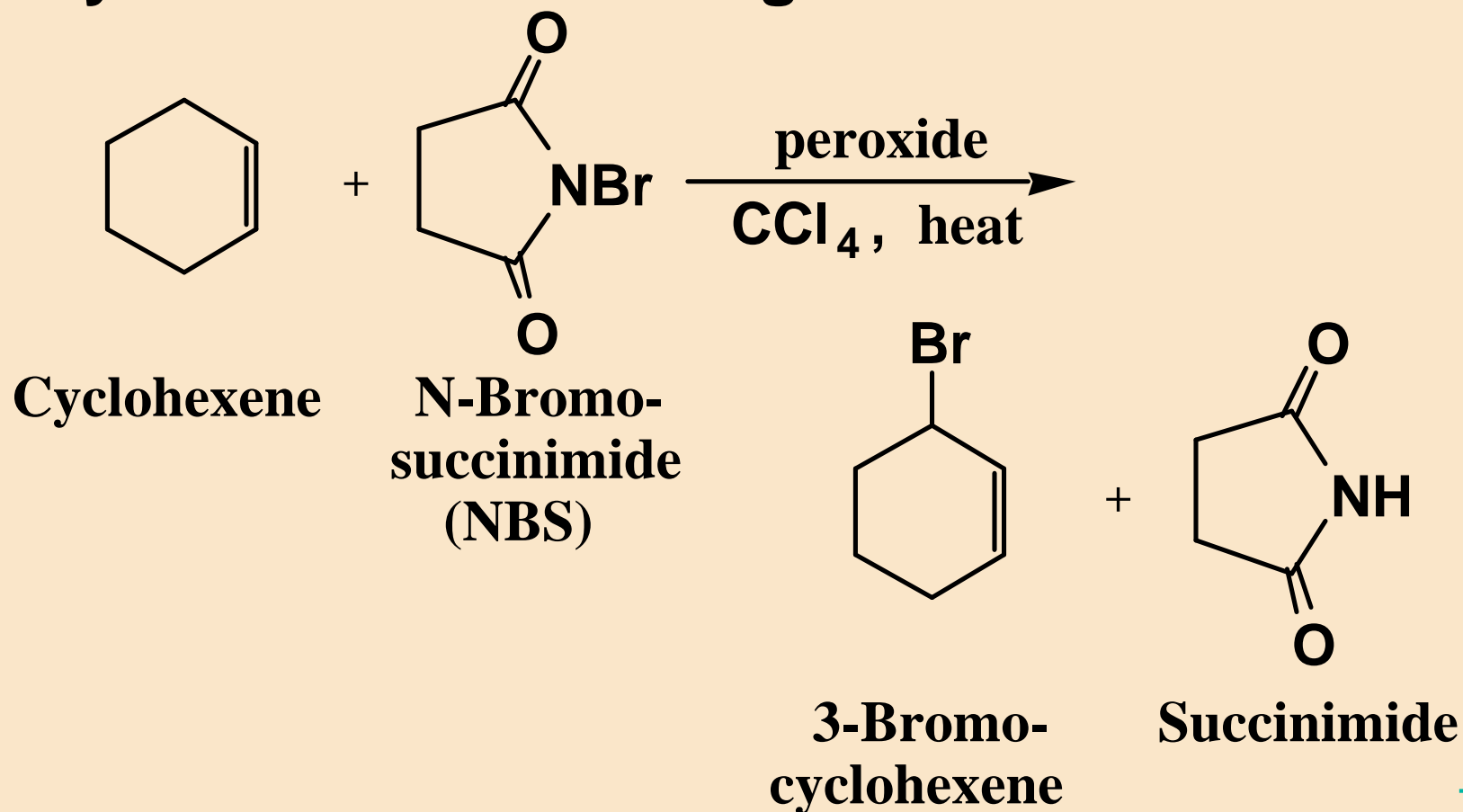
7 Allylic Halogenation

- u An allylic C-H bond is weaker than a vinylic C-H bond



7 Allylic Bromination

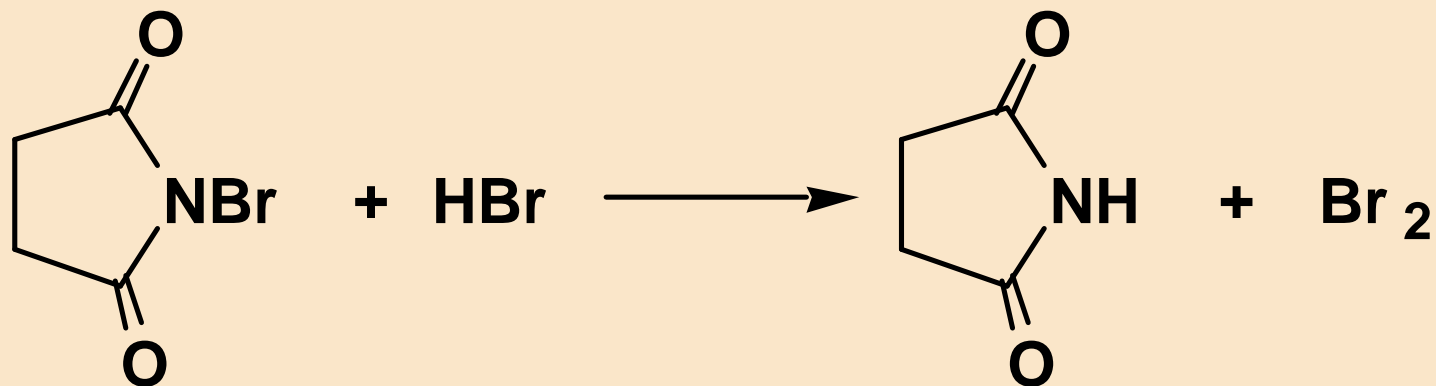
u Allylic bromination using NBS



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7 The Function of NBS

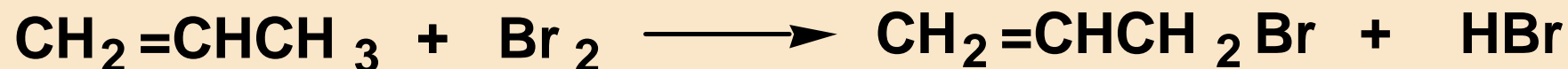
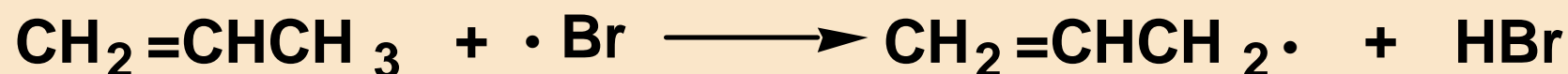
- u The Br_2 necessary for radical halogenation is provided by reaction of NBS with HBr



7 Allylic Bromination

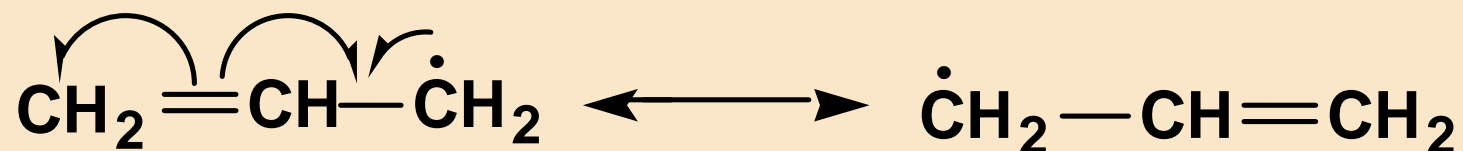
u A radical chain mechanism

Chain propagation:



7 The Allyl Radical

u A hybrid of two equivalent contributing structures



(Equivalent contributing structures)

7 Organometallic Cmpds

- u **Organometallic compound:** a compound that contains a metal bonded to a carbon atom



An organomagnesium
compound
(a Grignard reagent)



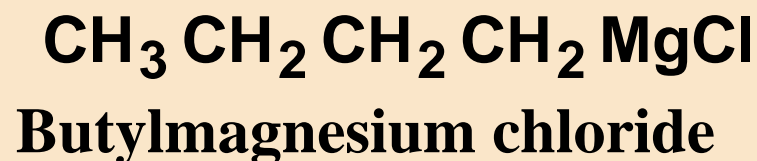
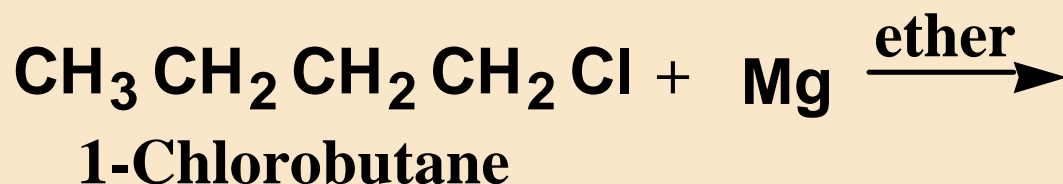
A lithium
diorganocopper compound
(a Gilman reagent)



An organolithium
compound

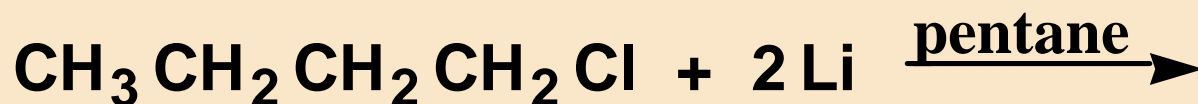
7 Organometallic Cmpds

- u Grignard reagents are formed by reaction of an alkyl halide with magnesium metal in diethyl ether or tetrahydrofuran (THF)

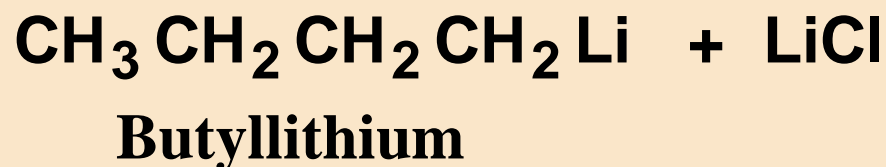


7 Organometallic Cmpds

- u Organolithium reagents are formed by reaction of an alkyl halide with lithium metal in a hydrocarbon solvent such as pentane



1-Chlorobutane



7 Organometallic Cmpds

u Carbon-metal bonds are polar covalent

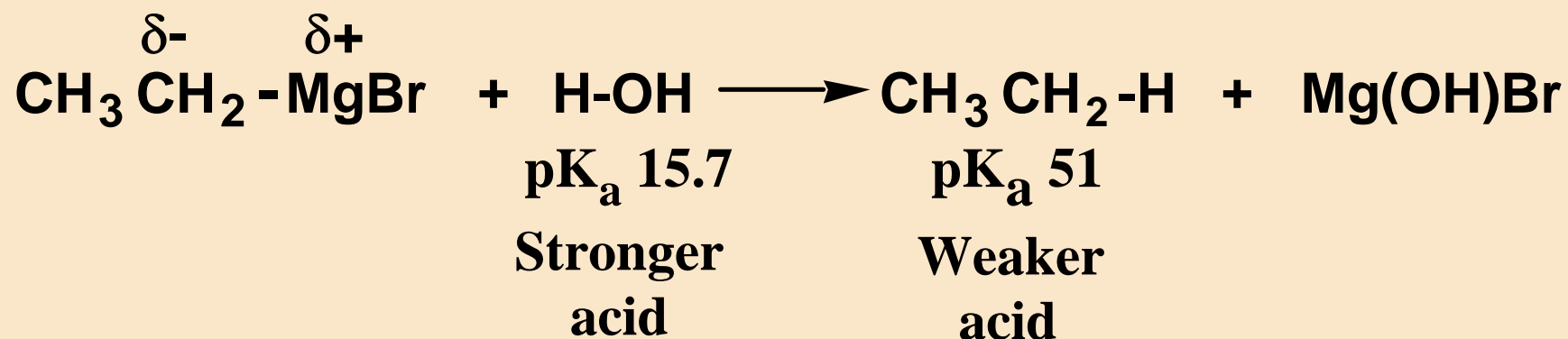
C-M Bond	Difference in Electronegativity	Percent Ionic character*
C-Li	2.5 - 1.0 = 1.5	60
C-Mg	2.5 - 1.2 = 1.3	52
C-Zn	2.5 - 1.6 = 0.9	36
C-Cu	2.5 - 1.9 = 0.6	24
C-Hg	2.5 - 1.9 = 0.6	24

$$\text{*Percent ionic character} = \frac{E_C - E_M}{E_C} \times 100$$

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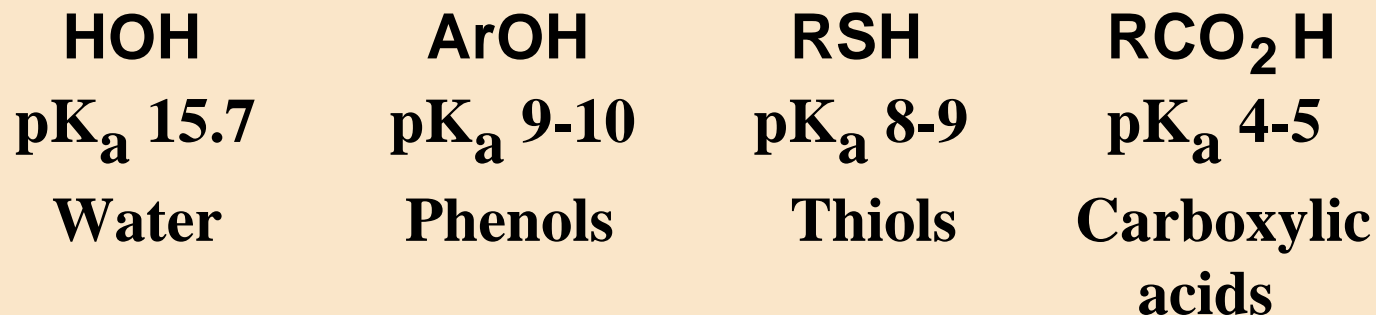
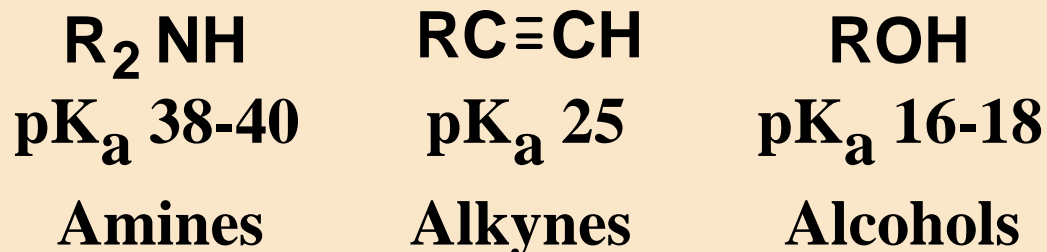
7 Organometallic Cmpds

- u Organometallics are strong bases and react with any proton donor stronger than the alkane from which they are derived



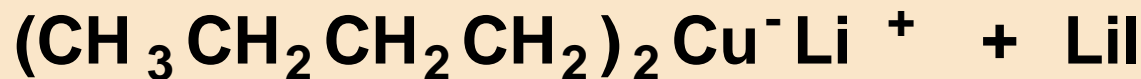
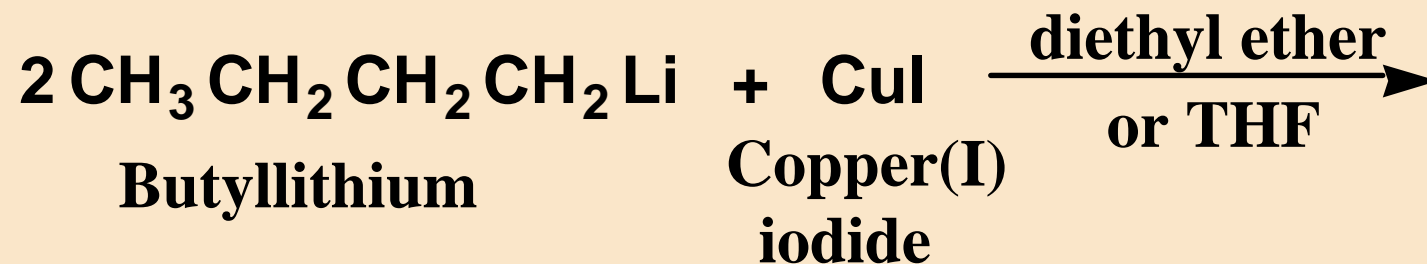
7 Organometallic Cmpds

u Classes of proton donors that react with Grignard and organolithium reagents are



7 Gilman Reagents

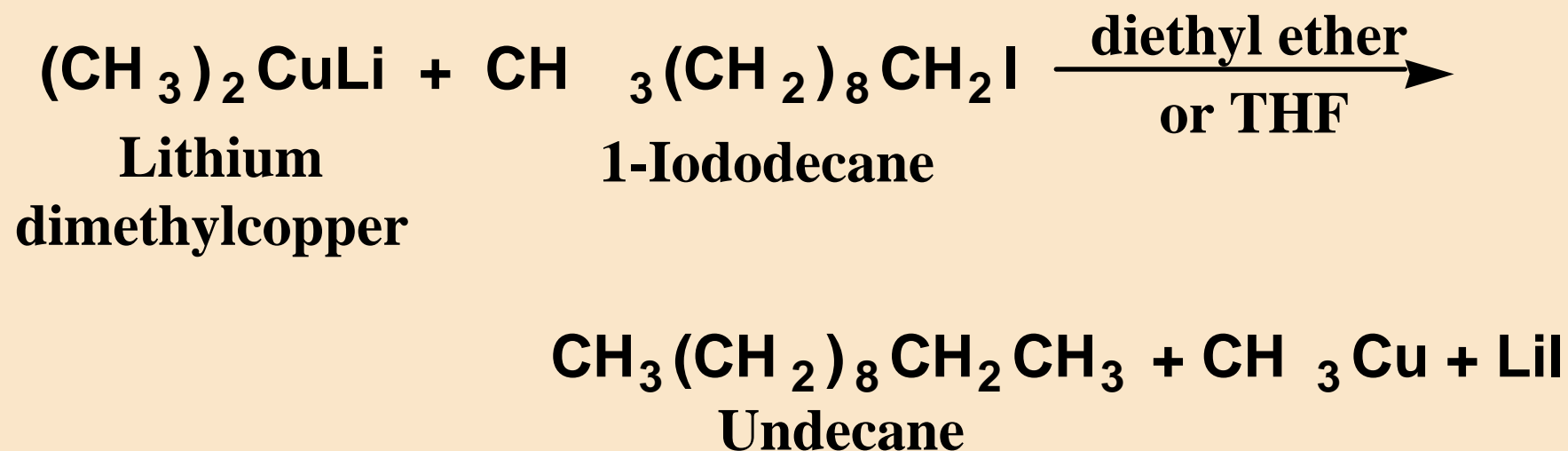
- u Prepared from an organolithium reagent and copper(I) iodide



Lithium dibutylcopper
(a Gilman reagent)

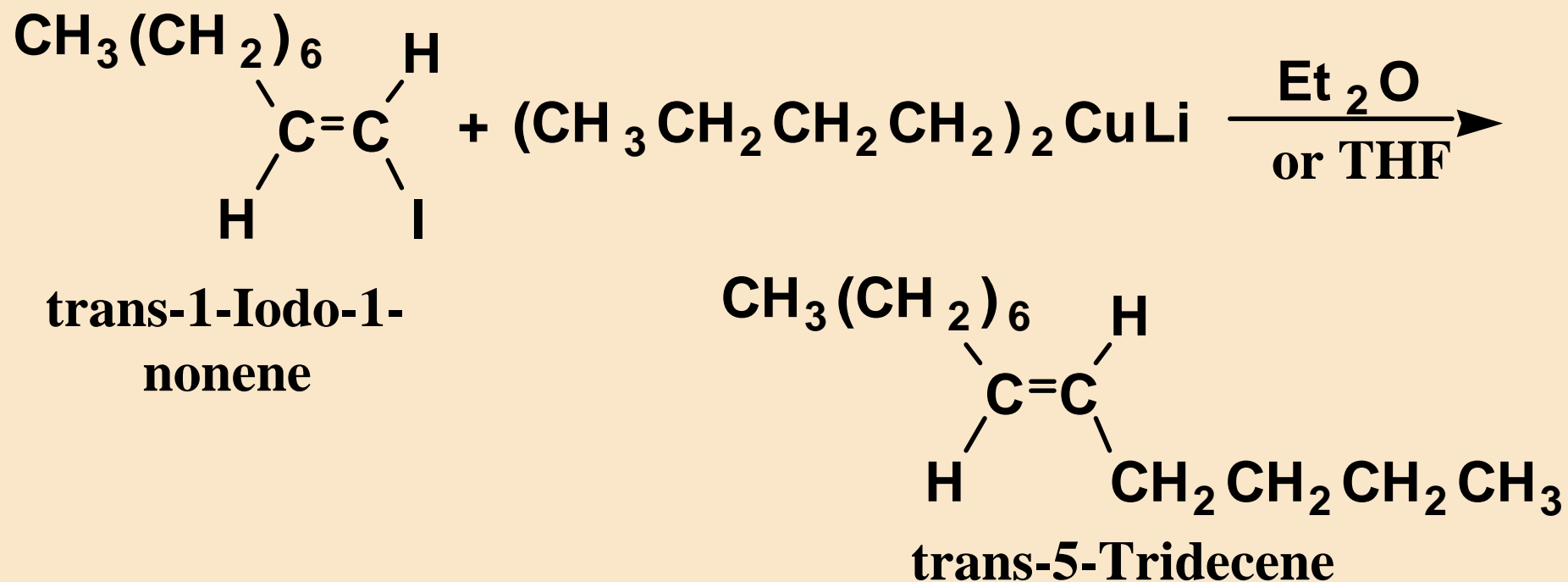
7 Gilman Reagents

- u Gilman reagents can be used to form new carbon-carbon bonds by cross-coupling with alkyl or vinylic halides



7 Gilman Reagents

u Cross-coupling with a vinylic halide



7

Alkyl Halides

End Chapter 7

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