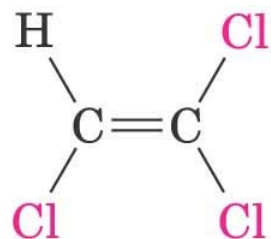


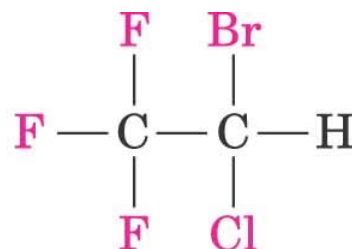
## 10. Alkyl Halides (R-X)

### What Is an Alkyl Halide?

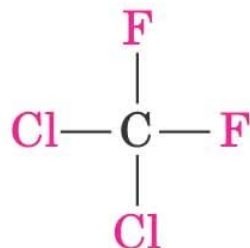
- An organic compound containing at least one carbon-halogen bond (C-X)
  - X (F, Cl, Br, I) replaces H
- Can contain many C-X bonds
- Properties and some uses
  - Fire-resistant solvents
  - Refrigerants
  - Pharmaceuticals and precursors



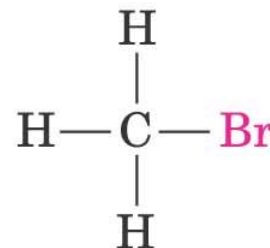
**Trichloroethylene**  
(a solvent)



**Halothane**  
(an inhaled anesthetic)



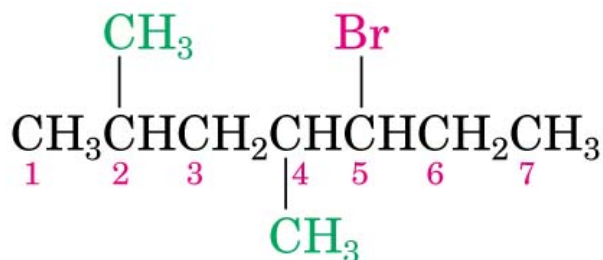
**Dichlorodifluoromethane**  
(a refrigerant)



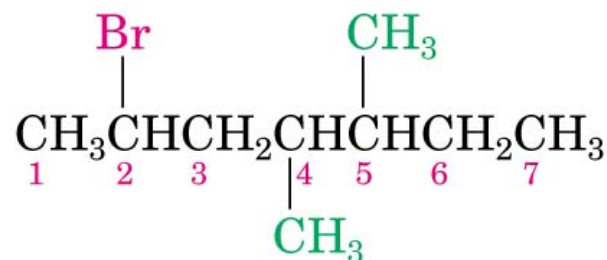
**Bromomethane**  
(a fumigant)

## 10.1 Naming Alkyl Halides

- Name is based on longest carbon chain
  - (Contains double or triple bond if present)
  - Number from end nearest any substituent (alkyl or halogen)

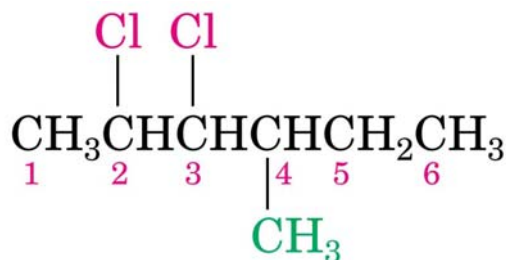


**5-Bromo-2,4-dimethylheptane**  
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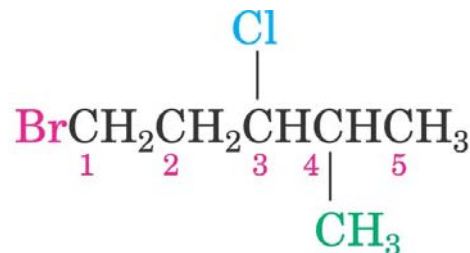


**2-Bromo-4,5-dimethylheptane**

- If more than one of the same kind of halogen is present, use prefix *di*, *tri*, *tetra*
- If there are several different halogens, number and list them in alphabetical order



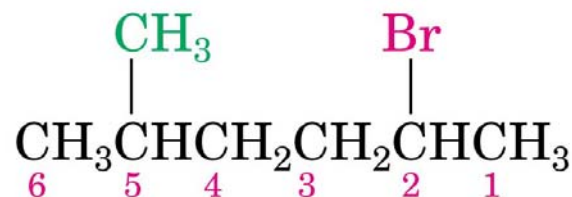
**2,3-Dichloro-4-methylhexane**  
© Thomson - Brooks Cole



**1-Bromo-3-chloro-4-methylpentane**  
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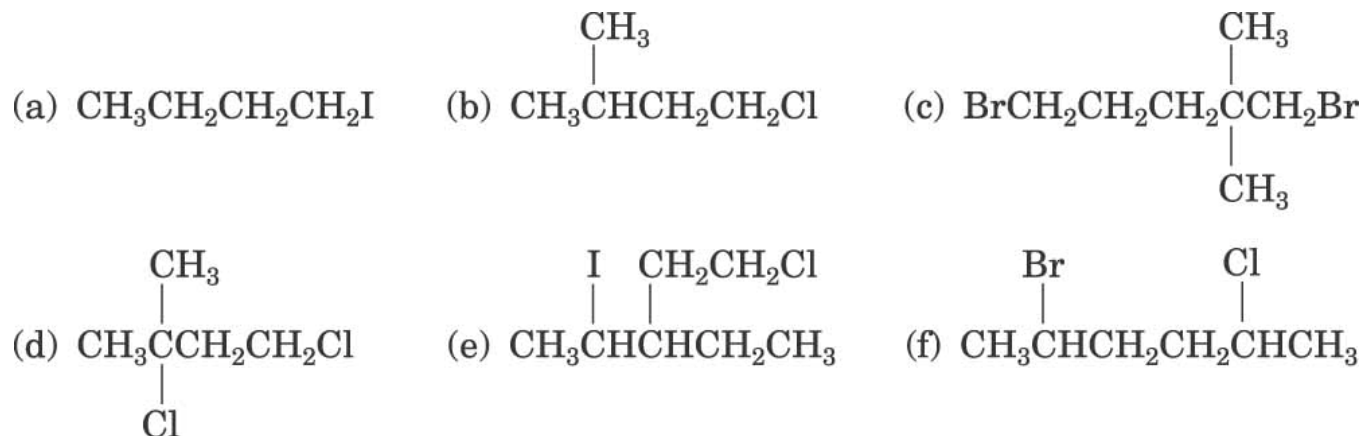
# Naming if Two Halides or Alkyl Groups Are Equally Distant from Ends of Chain

- Begin at the end nearer the substituent whose name comes first in the alphabet



**2-Bromo-5-methylhexane**  
**(NOT 5-bromo-2-methylhexane)**

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## 10.2 Structure of Alkyl Halides

- C-X bond is longer as you go down periodic table
- C-X bond is weaker as you go down periodic table
- C-X bond is polarized with slight positive on carbon and slight negative on halogen

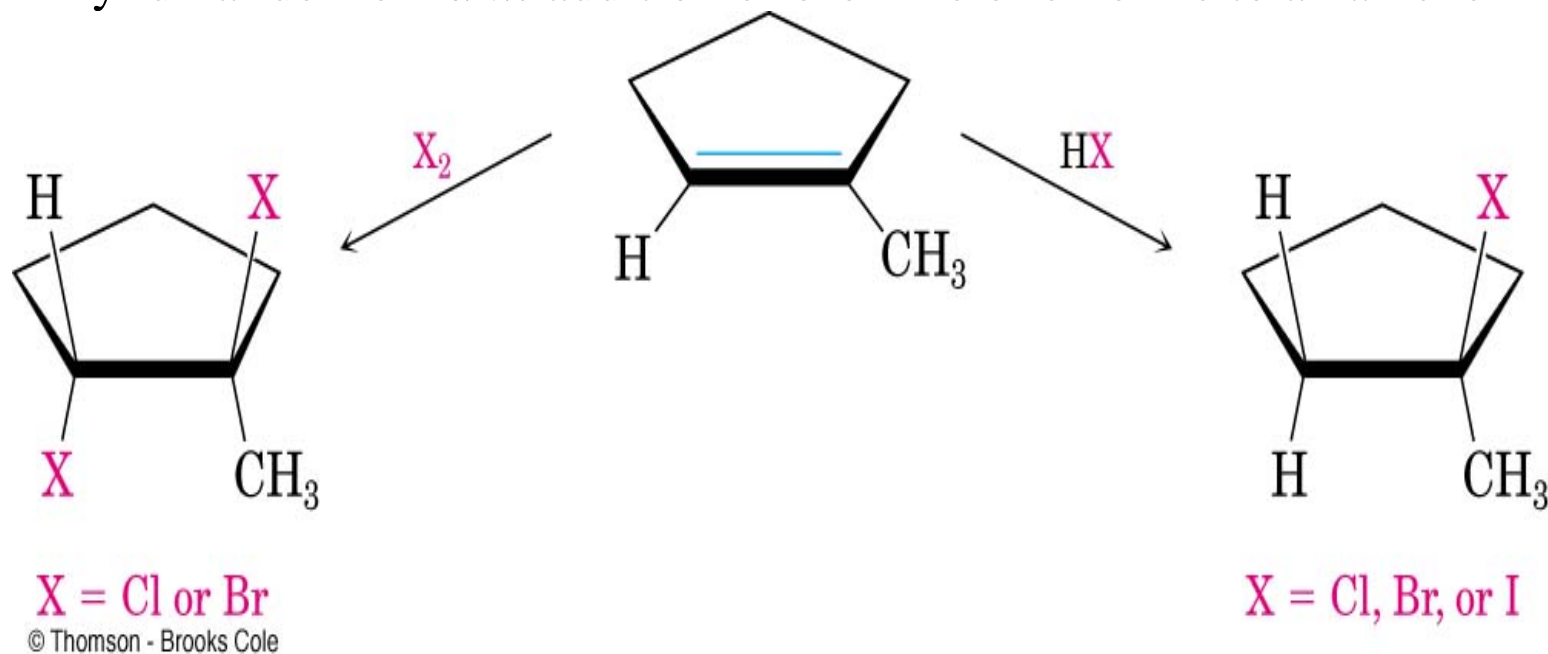
**TABLE 10.1** A Comparison of the Halomethanes

Halomethane	Bond length (pm)	Bond strength		Dipole moment ( <i>D</i> )
		(kJ/mol)	(kcal/mol)	
CH <sub>3</sub> F	139	452	108	1.85
CH <sub>3</sub> Cl	178	351	84	1.87
CH <sub>3</sub> Br	193	293	70	1.81
CH <sub>3</sub> I	214	234	56	1.62

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## 10.3 Preparation of Alkyl Halides

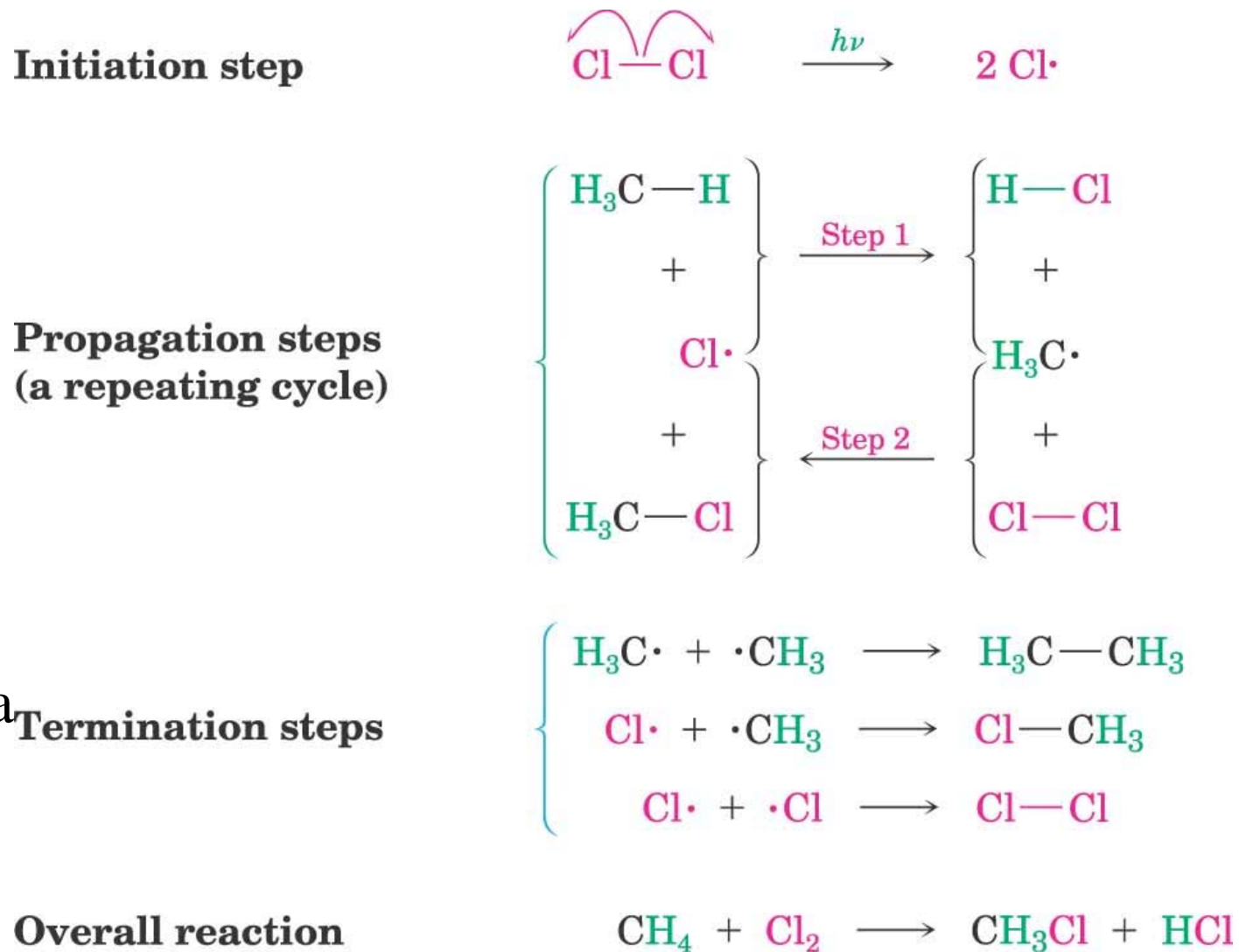
- Alkyl halide from addition of HCl, HBr, HI to alkenes to give Markovnikov product
- Alkyl dihalide from *anti* addition of bromine or chlorine to an alkene



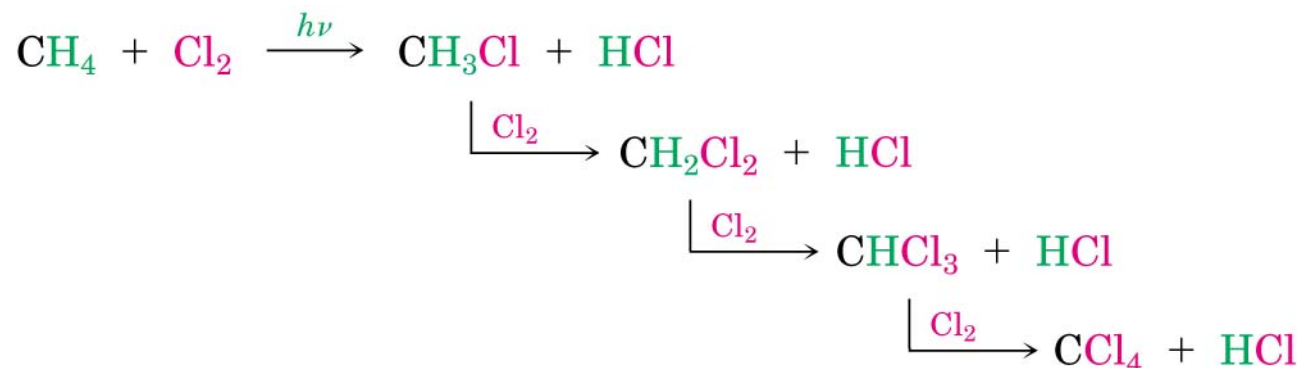
### Reaction of Alkanes with Halogens

- Alkane + Cl<sub>2</sub> or Br<sub>2</sub>, heat or light replaces C-H with C-X but Gives mixtures
  - Hard to control

- Via free radical mechanism (chain initiation, propagation & termination)
- See mechanism in Figure 10.1 (have seen in chapter 5)
- It is usually not a good idea to plan a synthesis that uses this method

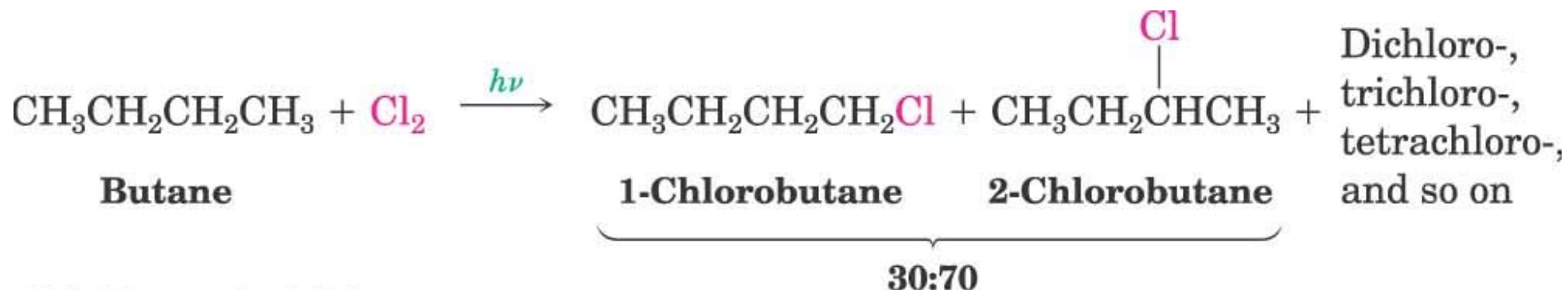


10.4 Ra

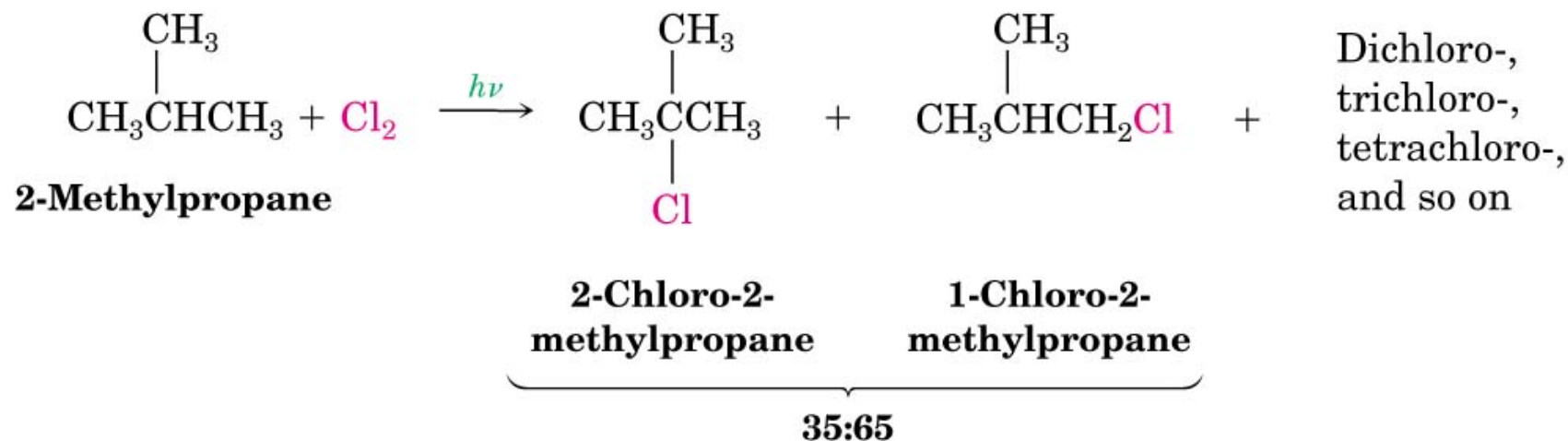


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- If there is more than one type of hydrogen in an alkane, reactions favor replacing the hydrogen at the most highly substituted carbons (not absolute)



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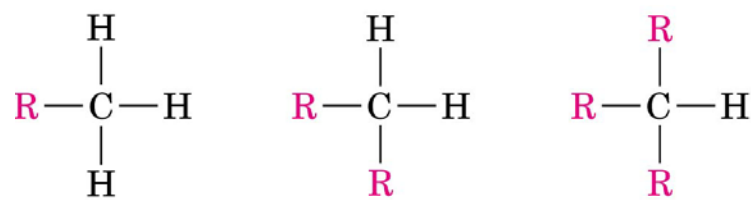
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There are 9 primary Hs and only 1 tertiary H, we would expect from probability calculations to have a 9:1 ratio!! Yet the ratio is 65:35, not even 2:1

## Relative Reactivity

- Based on quantitative analysis of reaction products, relative reactivity is estimated
- Order parallels stability of radicals
- Reaction distinction is more selective with bromine than chlorine (See Figure 10.2)

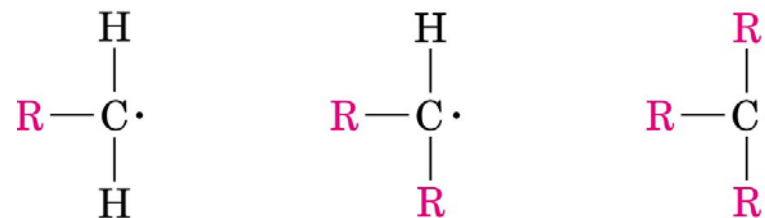




Primary 1.0 < Secondary 3.5 < Tertiary 5.0

Reactivity

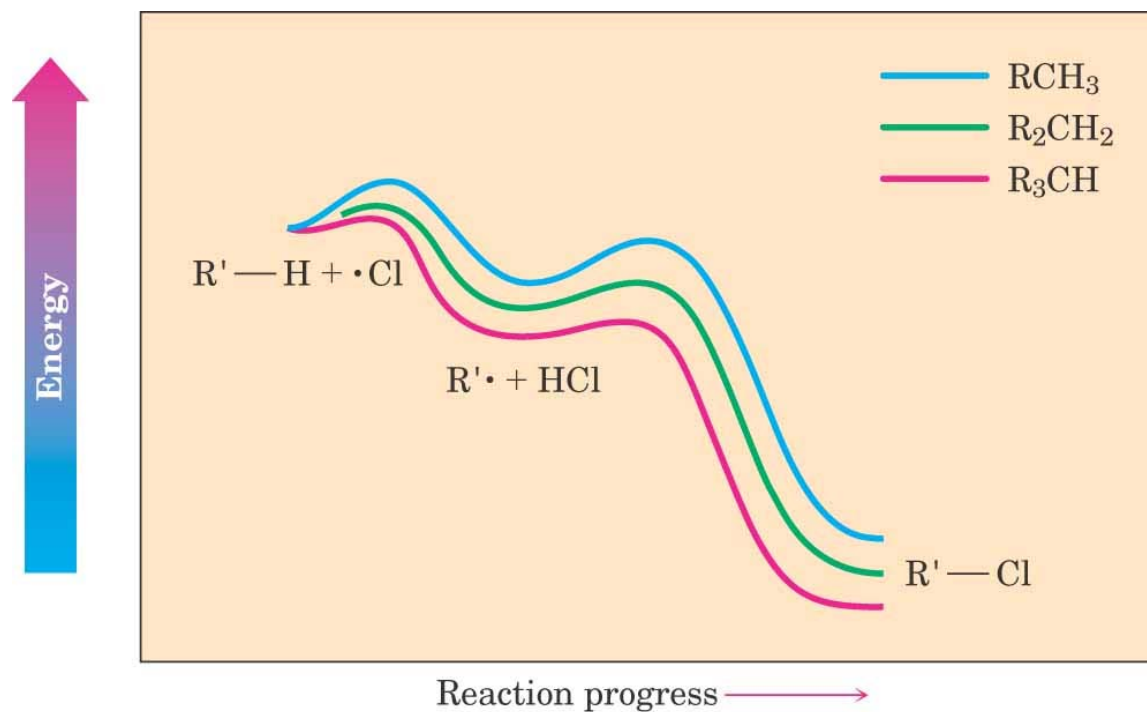
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Primary < Secondary < Tertiary

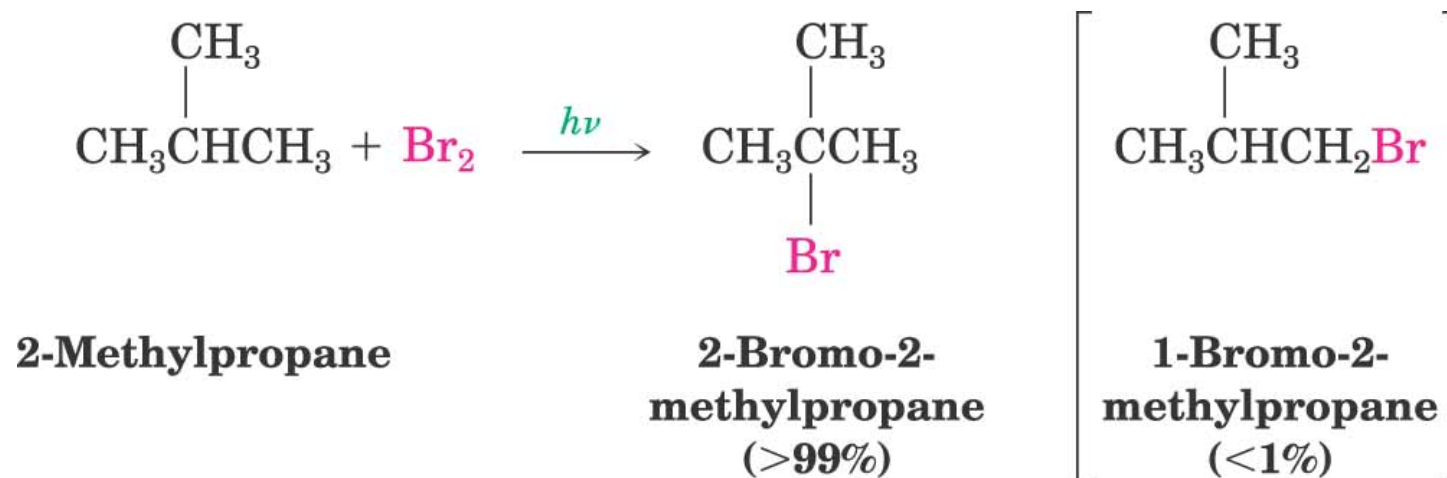
Stability

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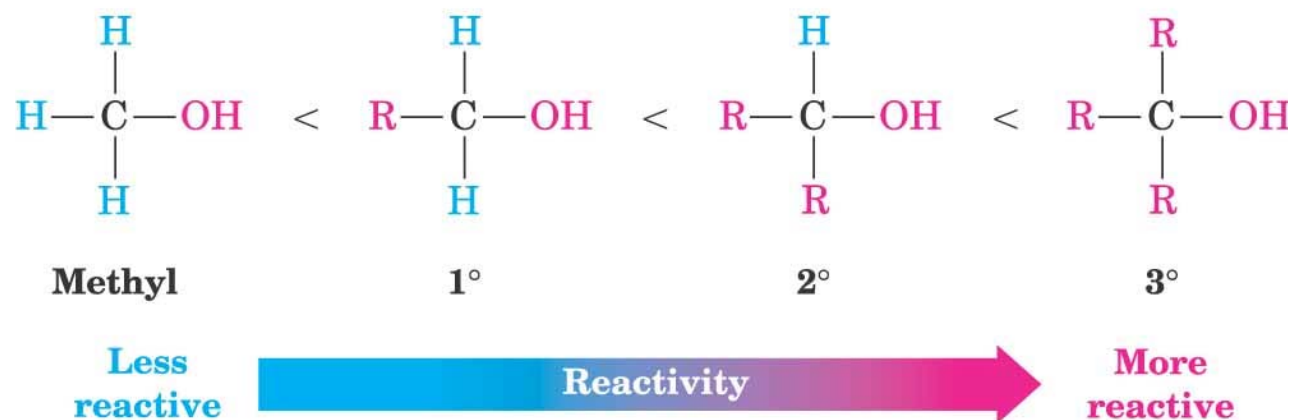
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Bromination is usually much more selective than chlorination (follows Hammond's postulate).



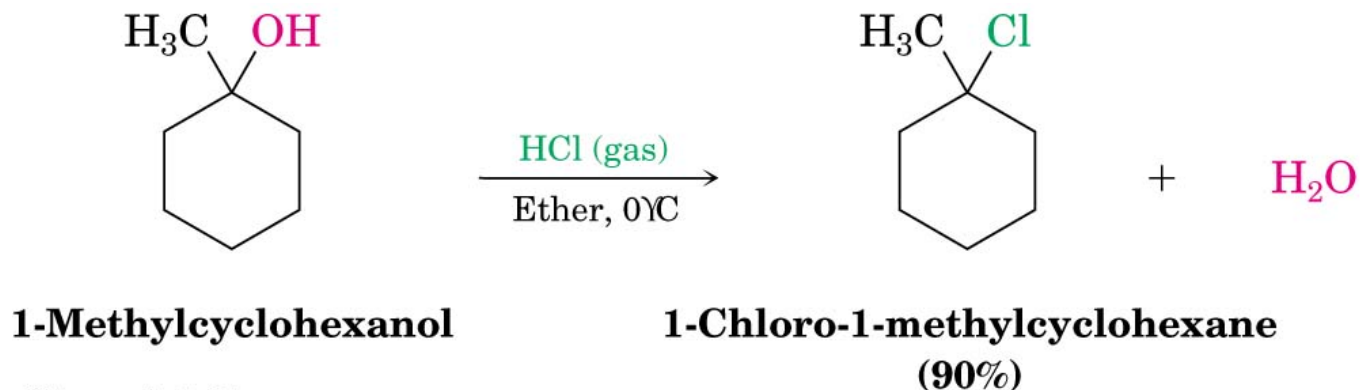
## 10.7 Preparation of Alkyl Halides from Alcohols

- Reaction of tertiary C-OH with HX is fast and effective
  - Add HCl or HBr gas into ether solution of tertiary alcohol
- Primary and secondary alcohols react very slowly and often rearrange, so alternative methods are used.



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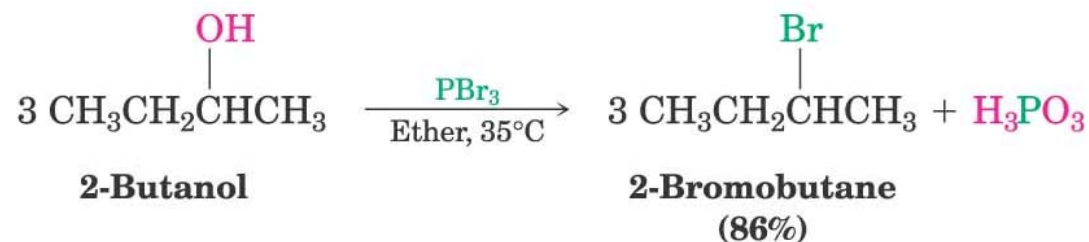
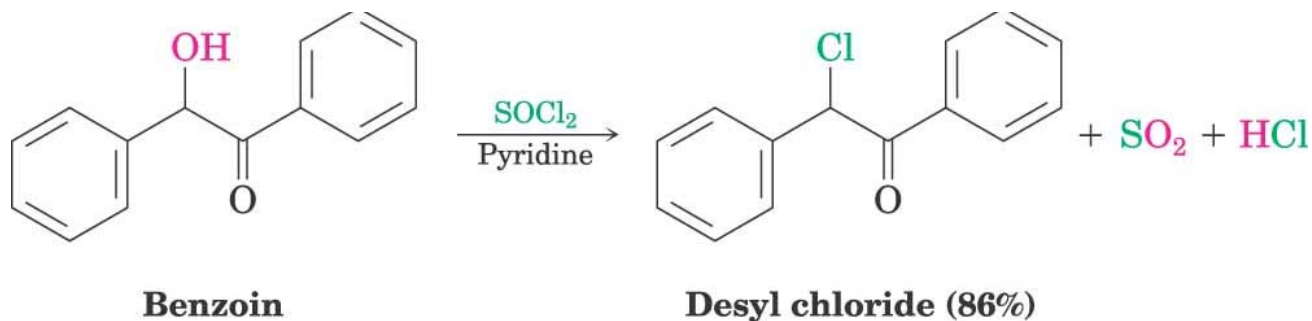
Mechanism?



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## Preparation of Alkyl Halides from Primary and Secondary Alcohols

- Specific reagents avoid acid and rearrangements of carbon skeleton
- Thionyl chloride converts alcohols into alkyl chlorides ( $\text{SOCl}_2$  :  $\text{ROH}$  to  $\text{RCl}$ )
- Phosphorus tribromide converts alcohols into alkyl bromides ( $\text{PBr}_3$ :  $\text{ROH}$  to  $\text{RBr}$ )



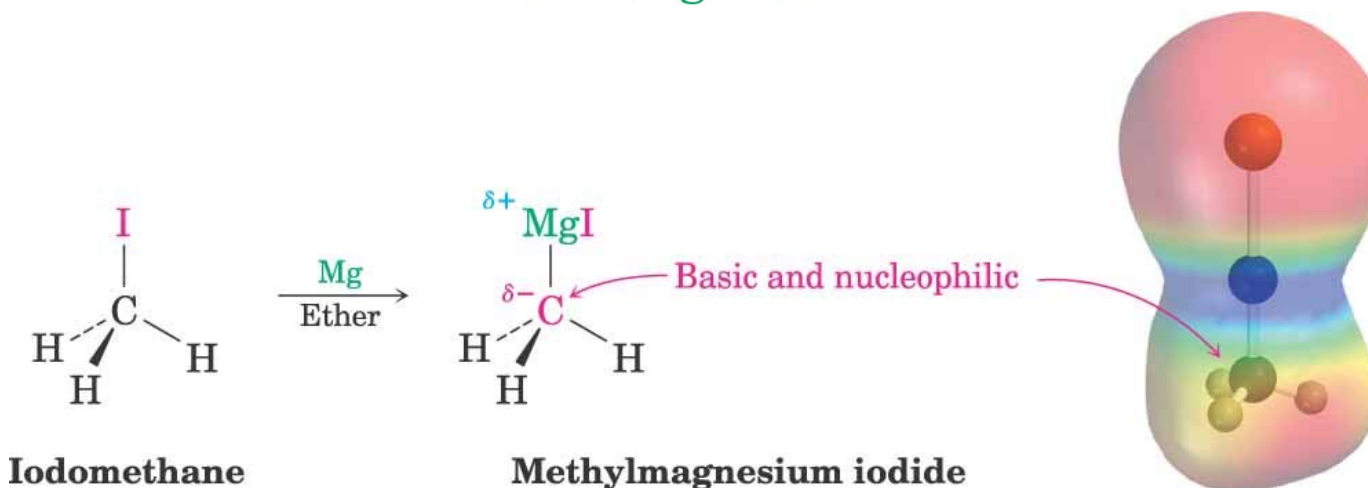
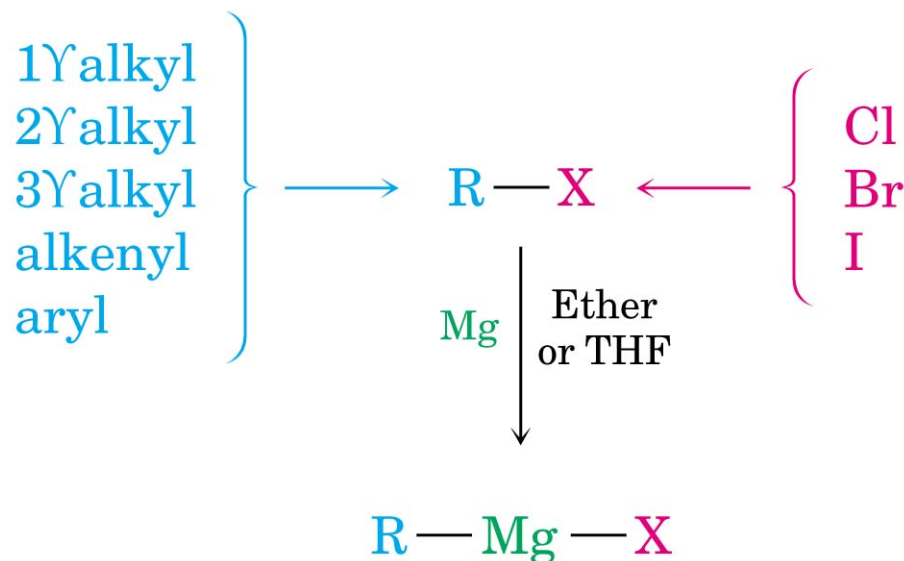
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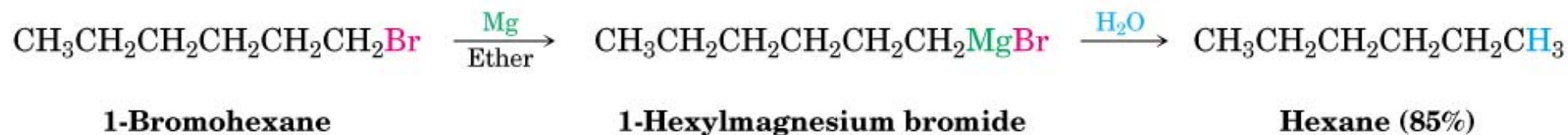
## 10.8 Reactions of Alkyl Halides: Grignard Reagents

■ Reaction of RX with Mg in ether or THF Produces RMgX – an organometallic compound (alkyl-metal bond)

■ R is alkyl 1°, 2°, 3°, aryl, alkenyl

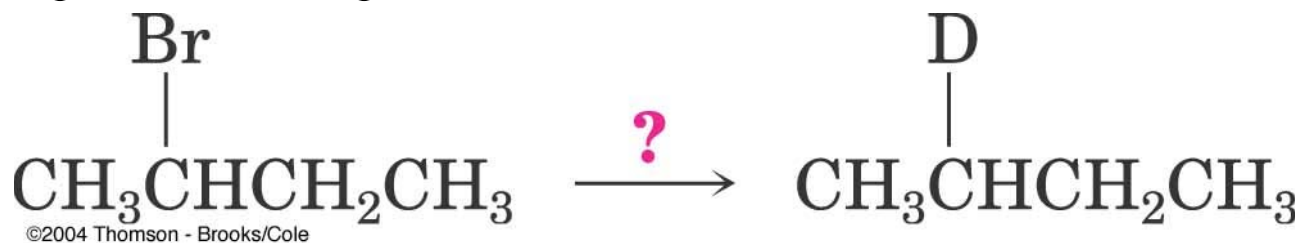
■ X = Cl, Br, I





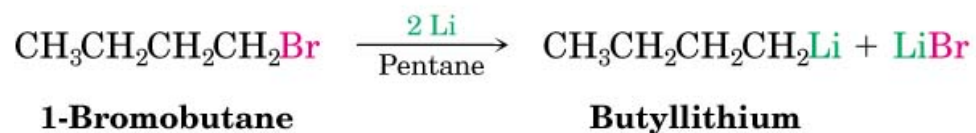
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- Many useful reactions from Grignard reagents
  - RMgX behaves as R<sup>-</sup> (nucleophilic carbon, adds to C=O to prepare alcohols))
  - RMgX + H<sub>3</sub>O<sup>+</sup> to give R-H

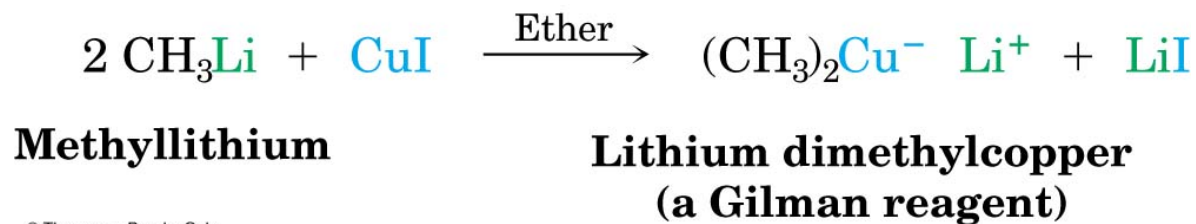
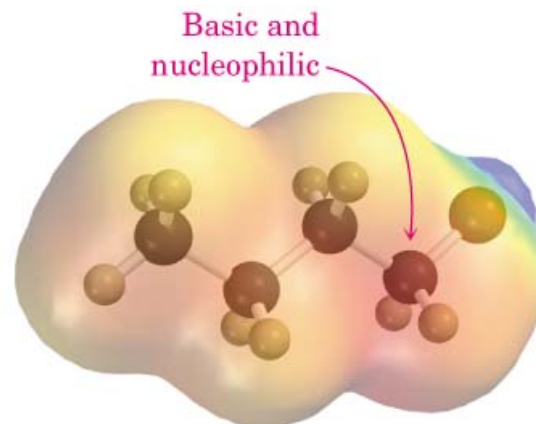


## 10.9 Organometallic Coupling Reactions

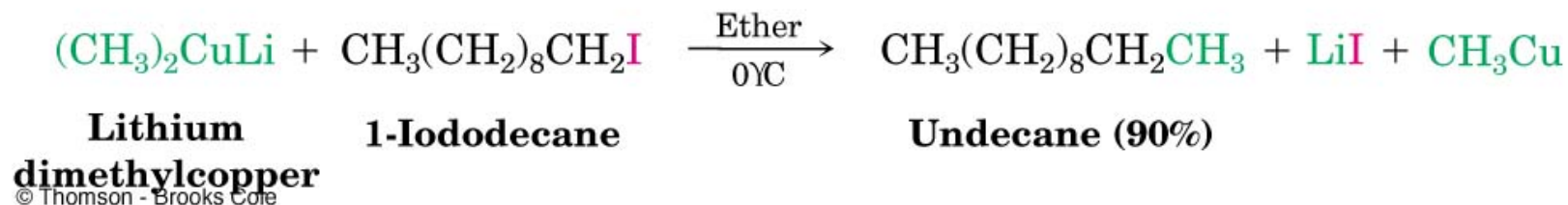
- Alkyl lithium (RLi) forms from RBr and Li metal
- RLi reacts with copper iodide to give lithium dialkylcopper (Gilman reagents)
- Lithium dialkylcopper reagents react with alkyl halides to give alkanes (making a C-C bond)



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A C-C bond was made (coupling) extending the length of a carbon chain by one carbon.

# Utility of Organometallic Coupling in Synthesis

- Coupling of two organometallic molecules produces larger molecules of defined structure
- Aryl and vinyl organometallics also effective
- Coupling of lithium dialkylcopper molecules proceeds through trialkylcopper intermediate

