# Preparation and Reactions of Organometallic Compounds

#### Reactions of Alkyl Halides:

- ✓ Substitution and elimination reactions:
- > Organometallic reagents and coupling reactions;
- > Reduction of alkyl halides.

Organolithium

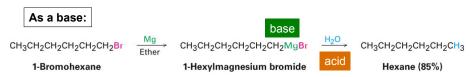
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>−Br + 2 Li hexane LiBr + CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>−Li

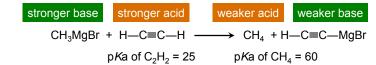
Grignard (Organomagnesium)

R-Mg-X

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### Reactions of Grignard Reagents





#### As a nucleophile:

$$R \longrightarrow RCH_2CH_2OMgBr \xrightarrow{H_2O} RCH_2CH_2OH$$

$$R \longrightarrow RCH_2CH_2OMgBr \xrightarrow{H_2O} RCOOH + HOMgB$$

$$R \longrightarrow RCOOH + HOMgB$$

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### Organometallic Coupling Reactions

 $\mathsf{CH_3CH_2CH_2CH_2-\!Li}$ 

BuLi is also basic and nucleophilic, and reacts with acids and electrophilies.

Gilman reagents (Organocuprates)

### transmetallation

$$R-X + [R'-Cu-R']^- Li^+ \longrightarrow \begin{bmatrix} R \\ I \\ R'-Cu-R' \end{bmatrix} \longrightarrow R-R' + R'-Cu$$

### Reduction of Alkyl Halides

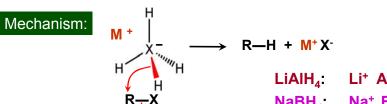
RX <del>H ⁻</del> RH

1. Using LiAlH<sub>4</sub> (a strongly reductive reagent):

- 1. Suitable for 1° and 2° alkyl halides; elimination occurs with 3° halides;
- 2. Reaction requires anhydrous conditions:

$$LiAlH_4 + 4H_2O \longrightarrow LiOH + Al(OH)_3 + 4H_2$$

- 2. Using NaBH<sub>4</sub> (a less strongly reductive reagent than LiAIH<sub>4</sub>):
- 1. Suitable for 2° and 3° alkyl halides; not competent for 1° halides;
- 2. Reaction takes place in basic aqueous solution.



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# Reduction of Alkyl Halides

Using HI or Zn + HCl:
$$CH_{3}(CH_{2})_{14}CH_{2}\overline{I} \xrightarrow{Zn + HCl} CH_{3}(CH_{2})_{14}CH_{3}$$

$$RX \xrightarrow{HI} RI \xrightarrow{HI} RH + I_{2}$$

#### Using H<sub>2</sub> / Pd-C (hydrogenolysis):

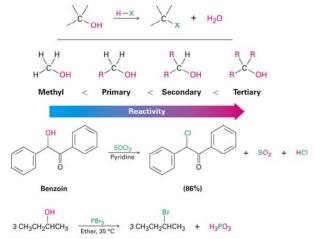
\* Suitable for benzyl halides, not for aliphatic halides.

#### Using Na (or Li) / NH<sub>3</sub> (liquid):

# Preparations of Alkyl Halides

> from alkanes: radical halogenation

> from alcohols:



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for 1° and 2° alcohols,

more commonly:

> from alkenes: subject of next chapter

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