Organometallic Compounds

(A) Grignard Reagents

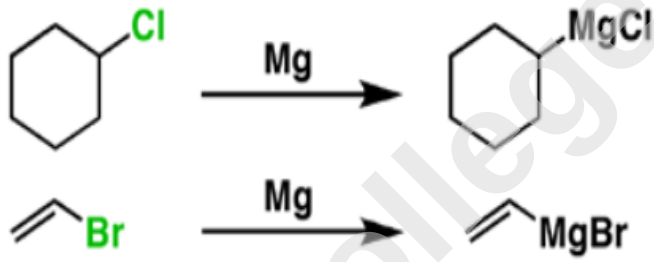
R–Mg–X

Also known as: Organomagnesium reagents

What it's used for: Extremely good nucleophile, reacts with electrophiles such as carbonyl compounds (aldehydes, ketones, esters, carbon dioxide, etc.) and epoxides. In addition Grignard reagents are very strong bases and will react with acidic hydrogens.

Similar to: Organolithium reagents (R–Li)

Example 1: Conversion of alkyl or alkenyl halides to Grignard reagents

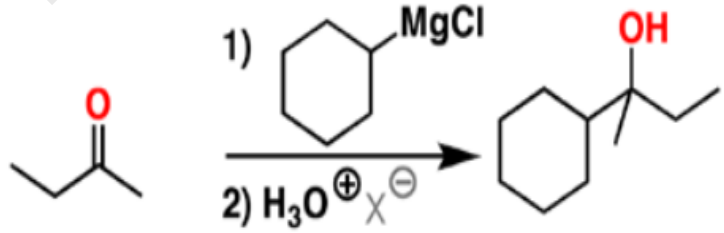


Grignards can be formed from alkyl or alkenyl chlorides, bromides, or iodides (never fluorides)

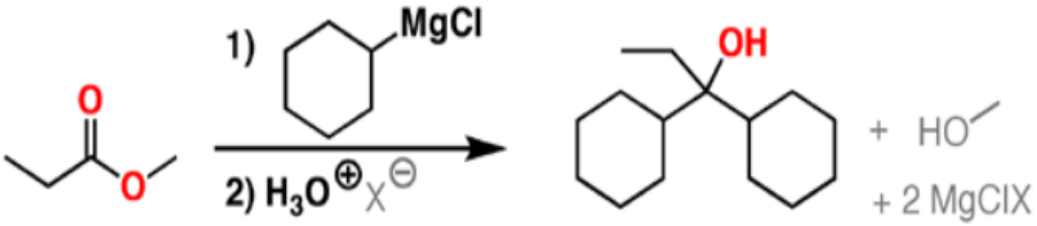
Example 2: Conversion of aldehydes to secondary alcohols

Acid is added in the second step to protonate the negatively charged oxygen.

Example 3: Conversion of ketones to tertiary alcohols

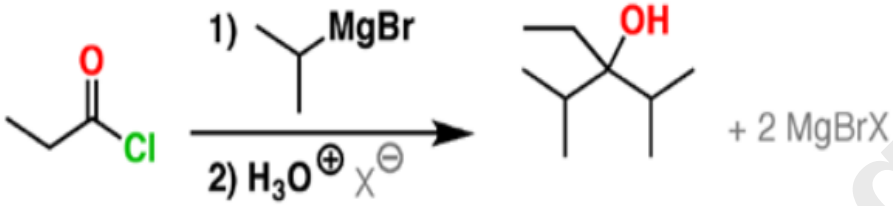


Example 4: Conversion of esters to tertiary alcohols

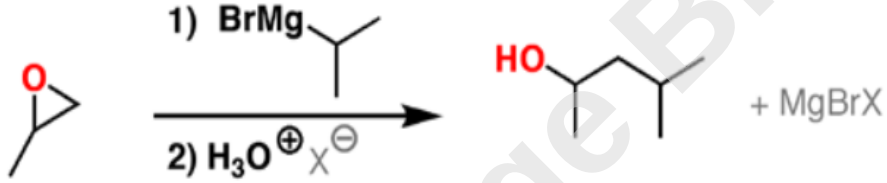


Grignard reagents add twice to esters, acid halides, and anhydrides

Example 5: Conversion of acyl halides to tertiary alcohols

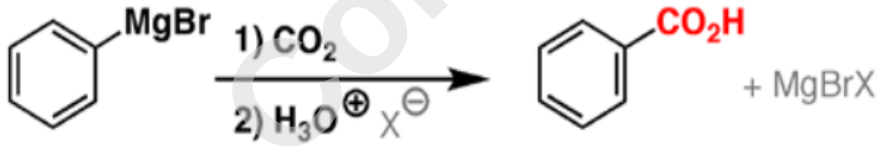


Example 6: Reaction with epoxides



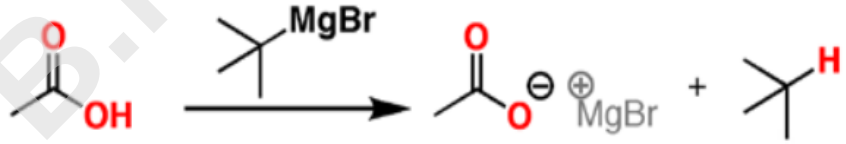
Grignard reagents add to the less substituted end of epoxides

Example 7: Reaction with carbon dioxide



The purpsoe of acid in the second step is to protonate the negatively charged oxygen.

Example 8: Reaction with acidic hydrogens



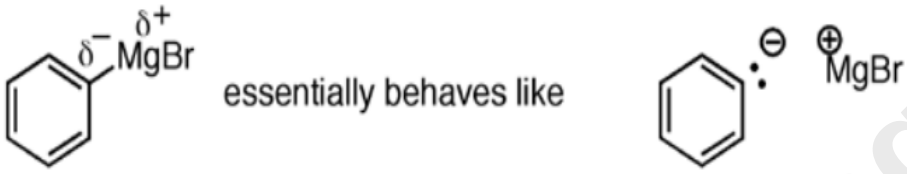
This can be used to introduce deuterium:

Deuterium is the heavy isotope of hydrogen

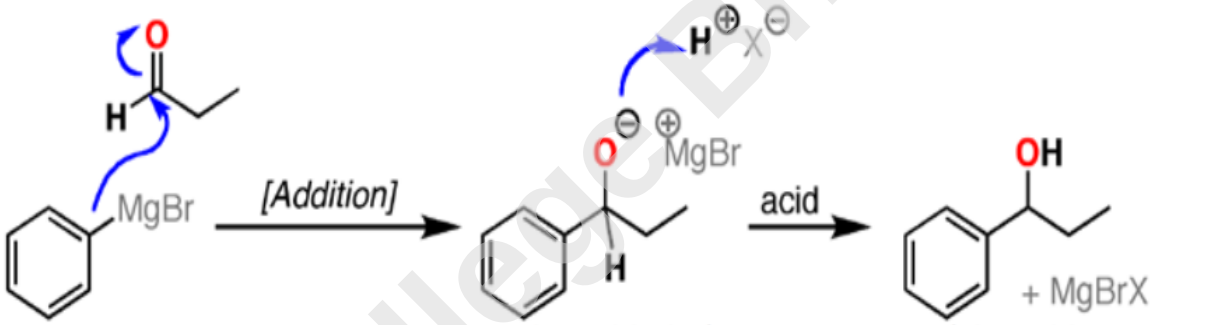
Mechanism:

How it works: ***Addition to aldehydes and ketones***

Grignard reagents are extremely strong nucleophiles. The electrons in the C–Mg bond are heavily polarized towards carbon

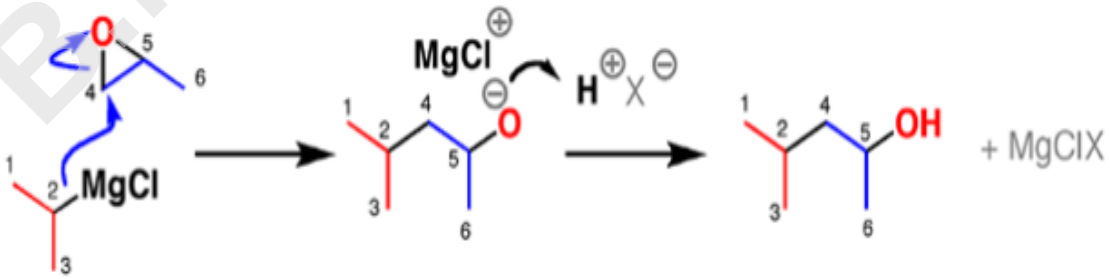


Therefore, Grignard reagents will react well with electrophiles such as aldehydes and ketones.



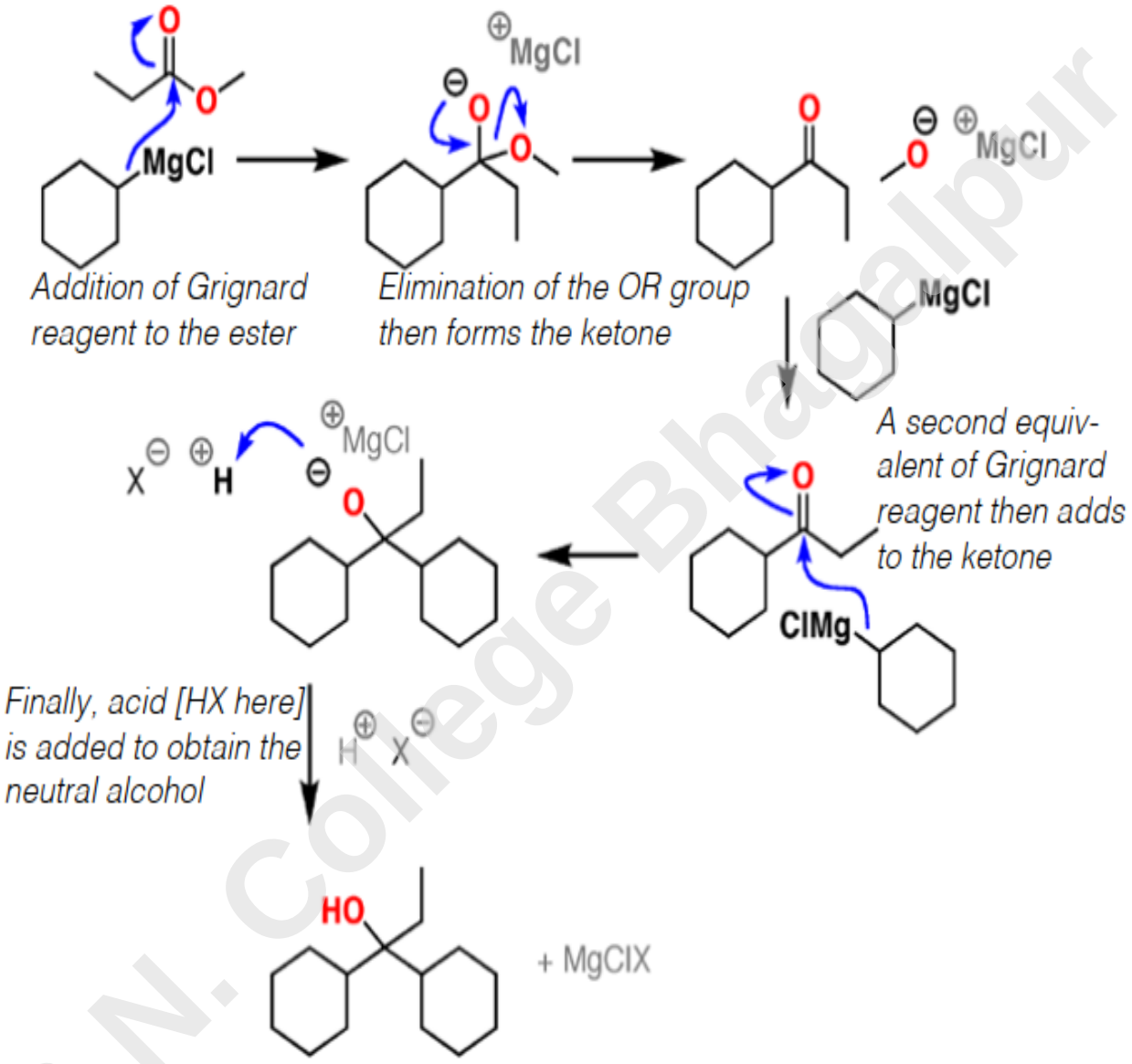
Acid is added after completion of the addition step

How it works: ***Addition to epoxides***

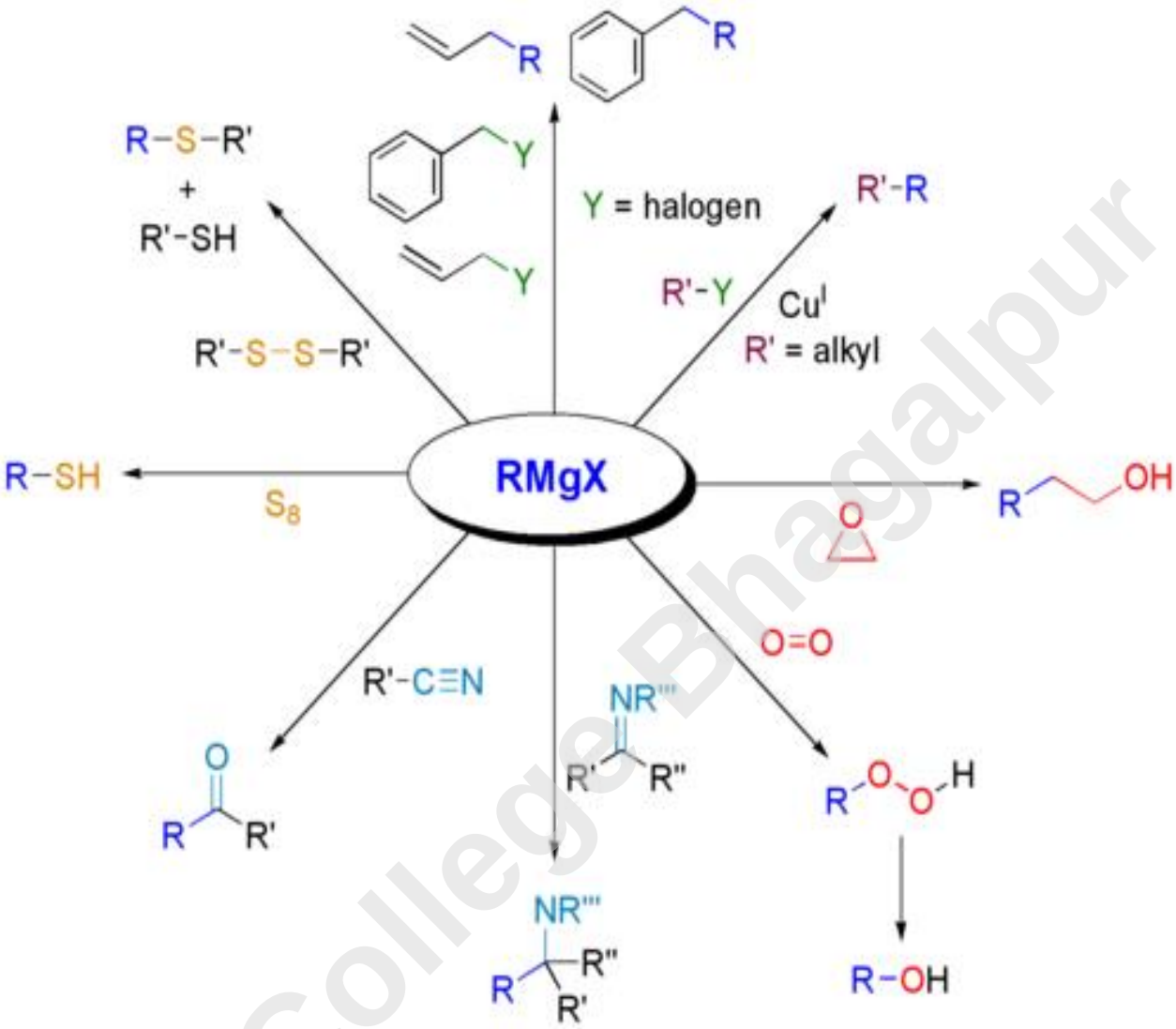


How it works: ***Addition to esters***

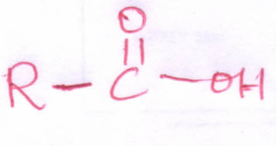
These proceed through a two step mechanism: addition followed by elimination. Acid is added at the end to obtain the alcohol.

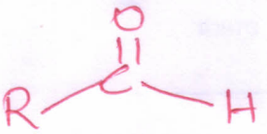


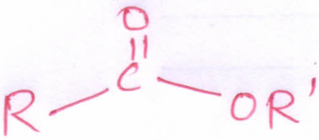
The same mechanism operates for acid halides and anhydrides.

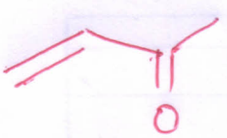


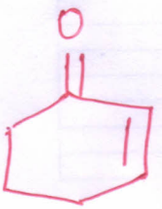
Questions:

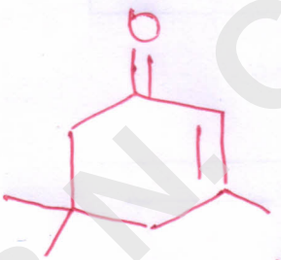
①  ① $R'MgBr$ ② H_3O^+

②  ① $R'MgBr$ ② H_3O^+

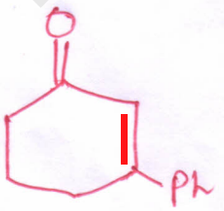
③  ① $2R''MgBr$ ② H_3O^+

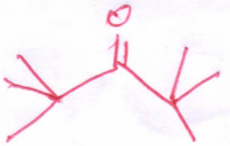
④  ① $MeMgBr$ ② H_3O^+

⑤  ① $MeMgBr/Et_2O$ ② H_3O^+

⑥  ① $MeMgBr$ ② H_3O^+

 ① $MeMgBr/CuI$ ② H_3O^+

⑦  ① $MeMgCl/CuCl$ ② 

⑧  ① $MeMgBr$ ② H_3O^+

① $PhCH_2CH_2-MgBr$ ② H_2O^+