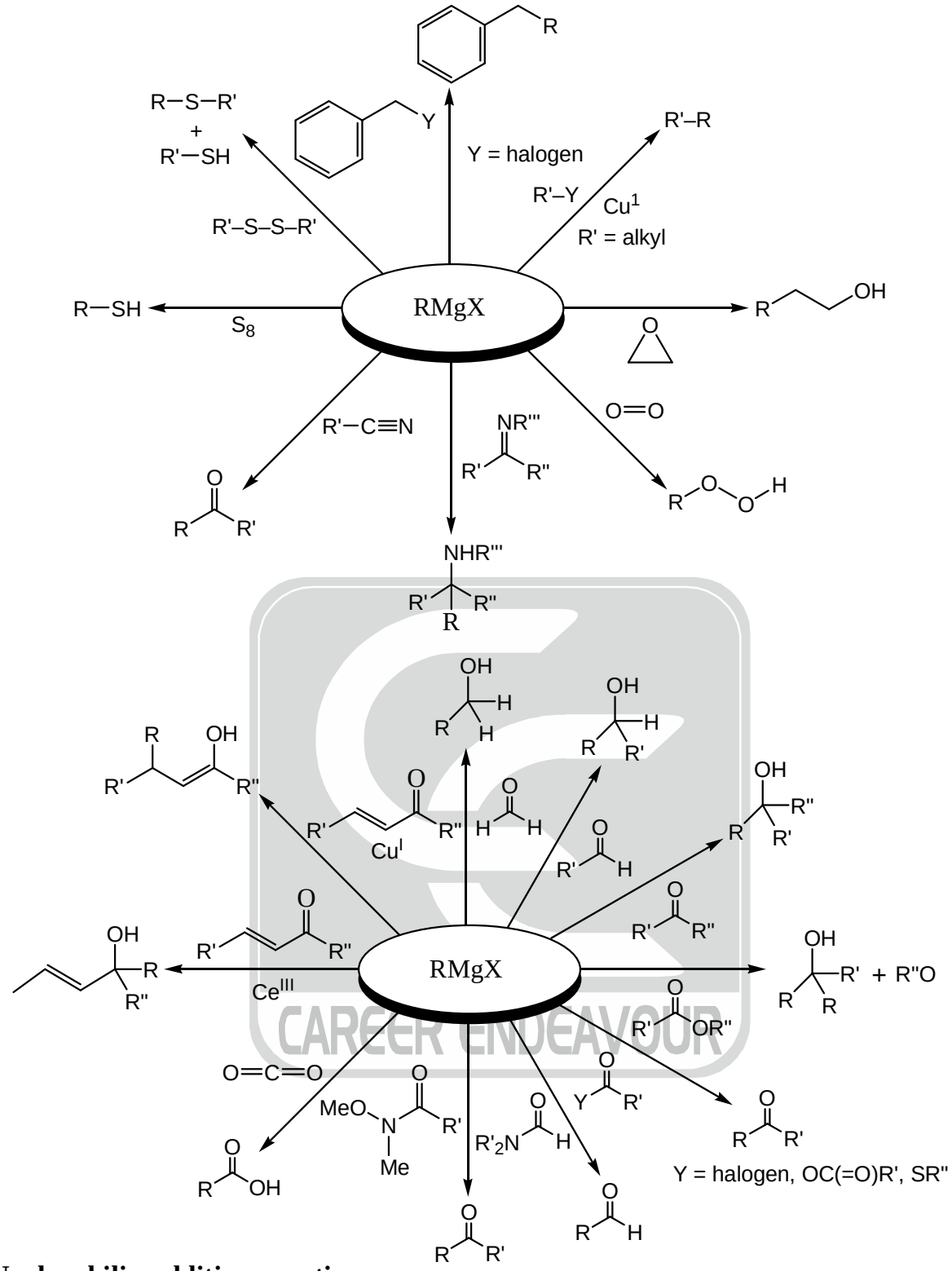
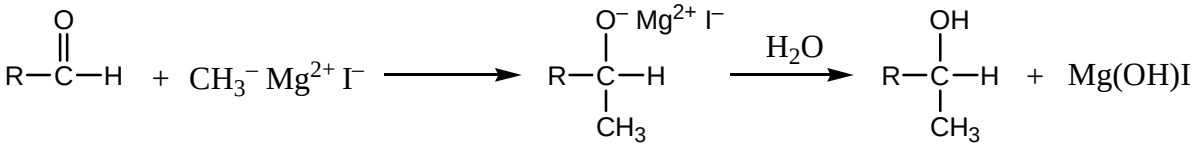



## Nucleophilic addition reactions:

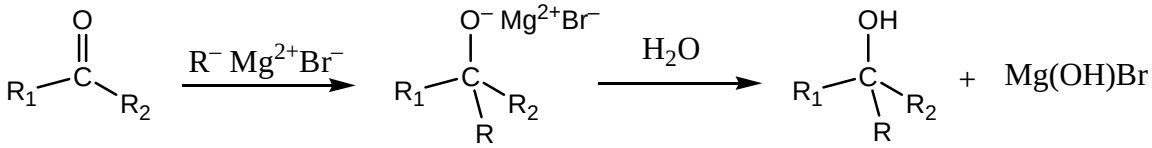
### Addition with aldehydes and ketones:

Aldehyde reacts with Grignard reagent to give addition products which on hydrolysis give primary alcohols.



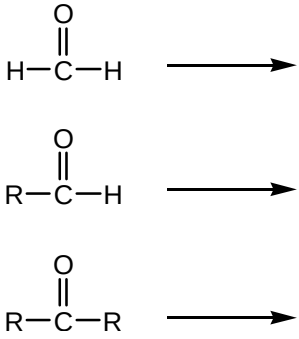

Where, R = H, alkyl, aryl

**Reaction with Ketone:**



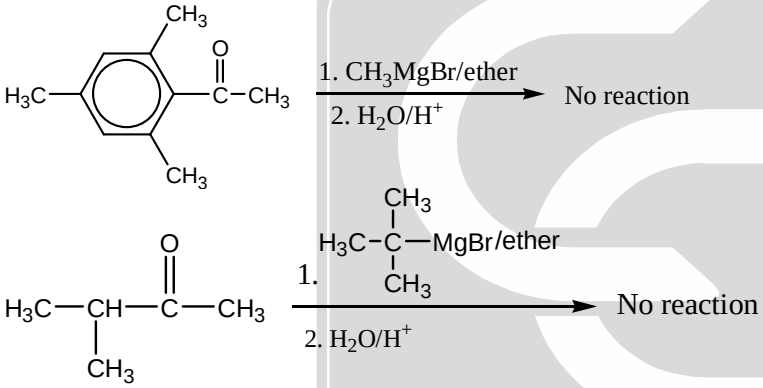

where, $R_1$ and $R_2$ may be alkyl or aryles

**Conclusion:**

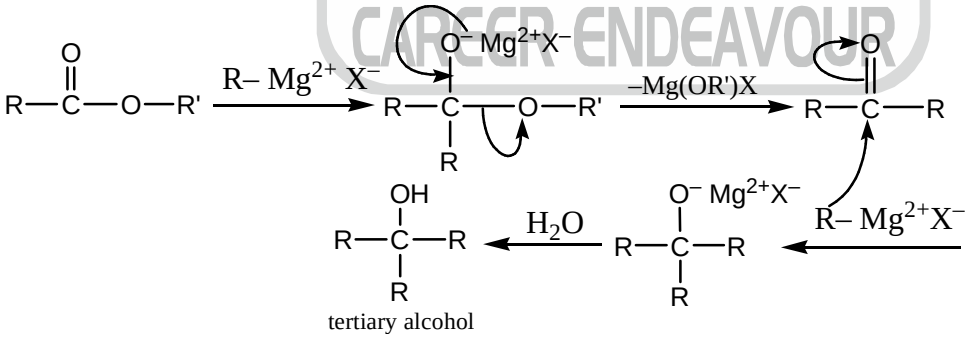



**Effect of steric hindrance:**

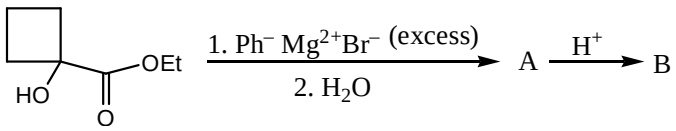
Grignard additions are influenced by the presence of bulky groups around the keto group or in Grignard reagent or in both.



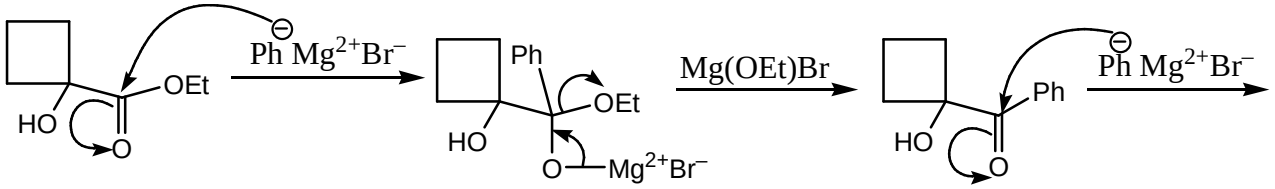

**Reaction with ester:**

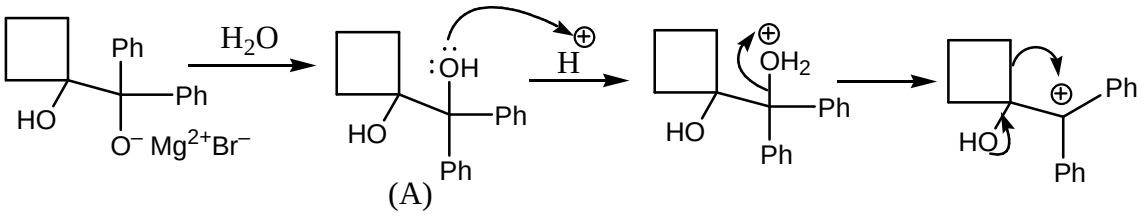



**Problem:**

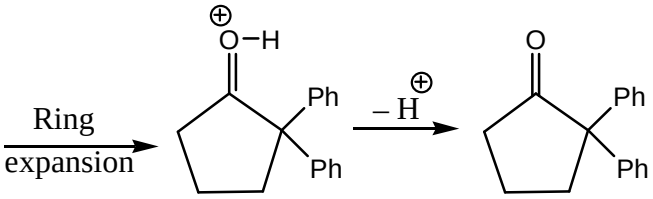



**Soln.**






(A)

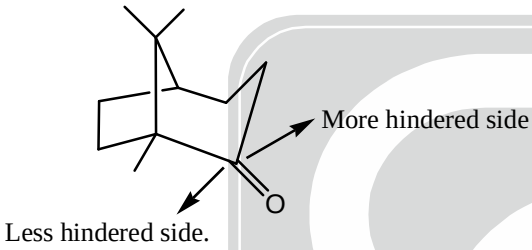



(B)

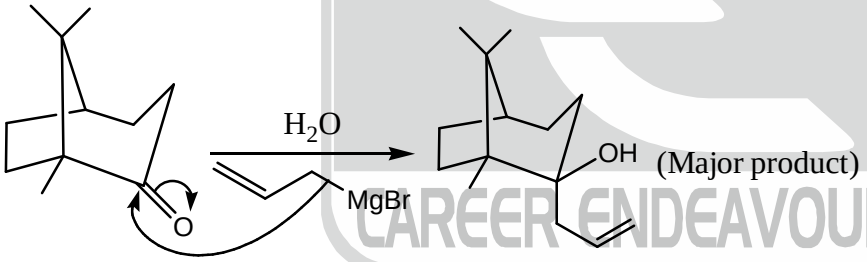
**Reaction with cyclic ketones:**

Reaction occurs through the less hindered side of the cyclic ketone.

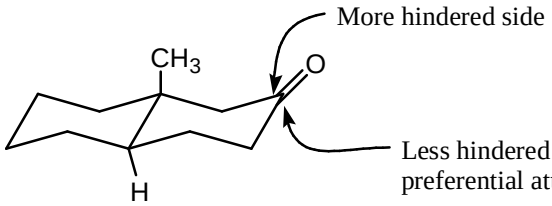
**Example:**

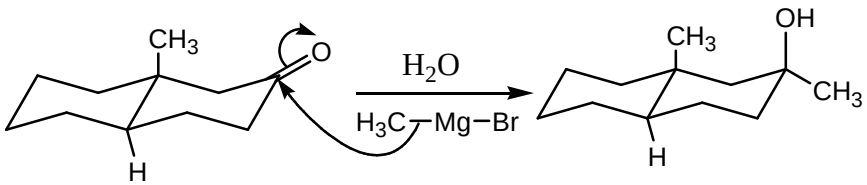



So, preferential attack, occur through less hindered side as shown below.



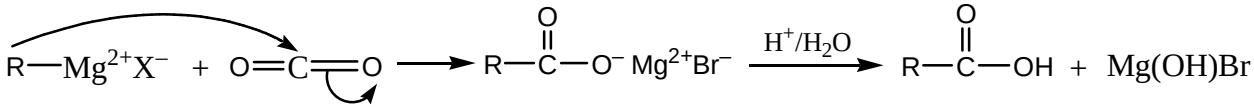


**Reaction with $CO_2$:**

Grignard reagent react with $CO_2$ to give addition products which on hydrolysis yield carboxylic acids.



**Reaction with inorganic halides:**

(1) $4C_2H_5MgBr + 2PbCl_2 \longrightarrow \underset{\text{Tetraethyl lead}}{(C_2H_5)_4Pb} + Pb + 4MgBr(Cl)$

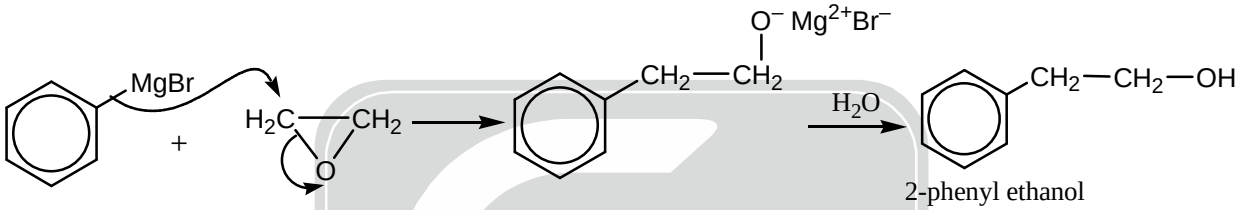
Ethyl magnesium bromide

(2) $4CH_3MgI + SiCl_4 \longrightarrow \underset{\text{(TMS)}}{(CH_3)_4Si} + 4MgI(Cl)$

(3) $2C_2H_5MgI + HgCl_2 \longrightarrow \underset{\text{Diethyl mercury}}{(C_2H_5)_2Hg} + 2MgICl$

Ethyl magnesium Iodide

**Reaction with epoxide:**

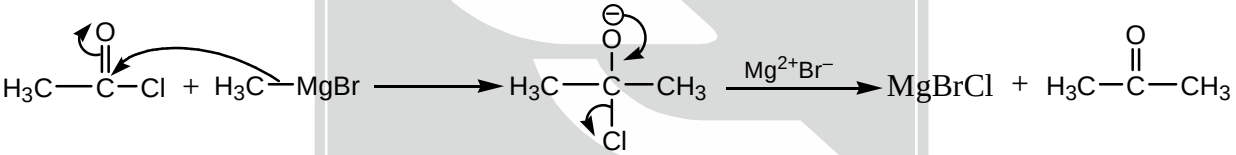


2-phenyl ethanol

**Note:** Nucleophilic attack generally occur at the less hindered carbon atom as the epoxide.

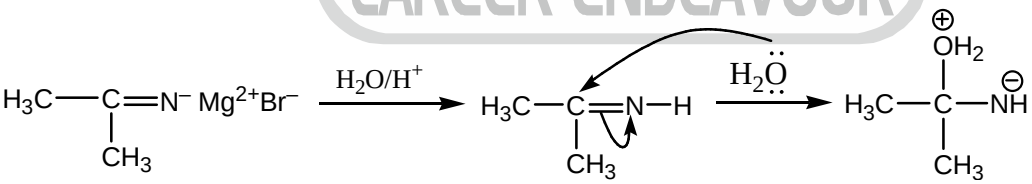
**Reaction with acid chloride:** Grignard reagents react with acid chlorides to form ketones.

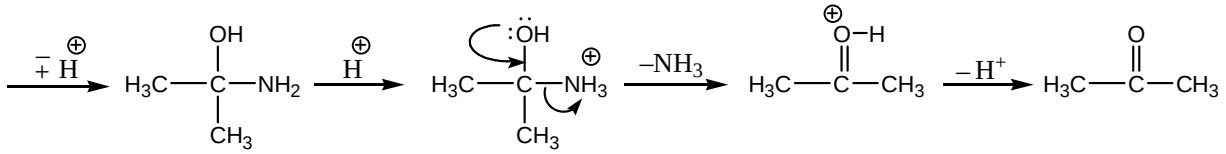
**For example:**



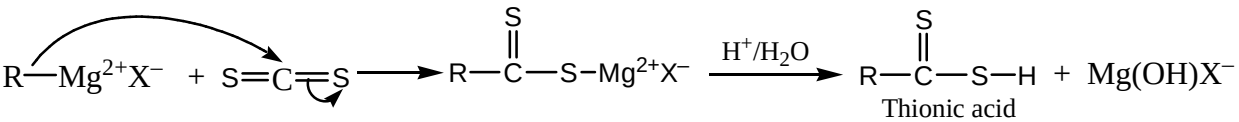
**Reaction with Amids:** Amids reaction with Grignard reagent yield ketones.

**Mechanism:**





**Reaction with $CS_2$:**



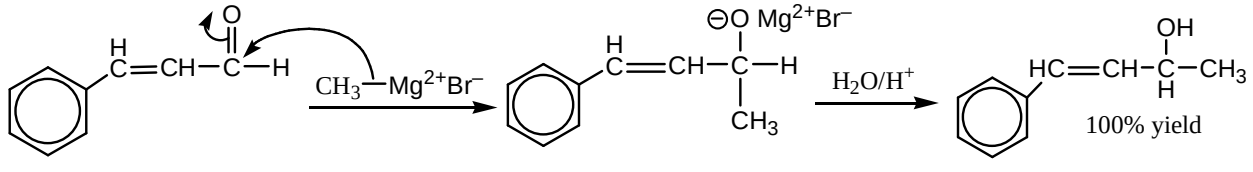
Thionic acid

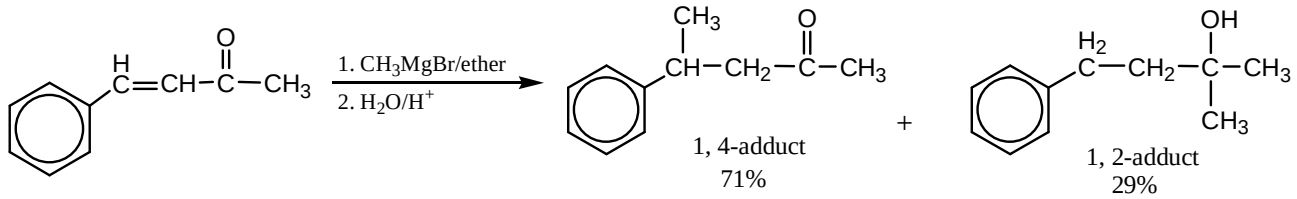
**Reaction with α, β-unsaturated aldehyde and ketones:**

Grignard reagents readily add to α-, β-unsaturated aldehyde and ketones, in such a reaction both 1, 2 and 1, 4-addition products are formed.

In general α-, β-unsaturated aldehydes give predominantly 1, 2-addition product and α-, β-unsaturated ketones give 1, 4-addition product as the major product.

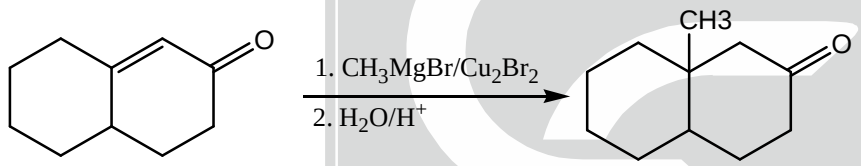
**Example:**

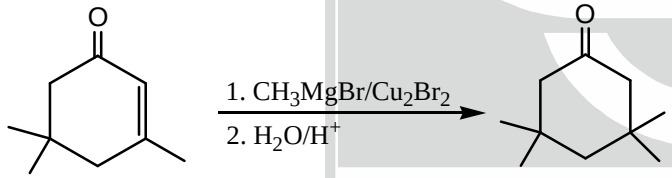


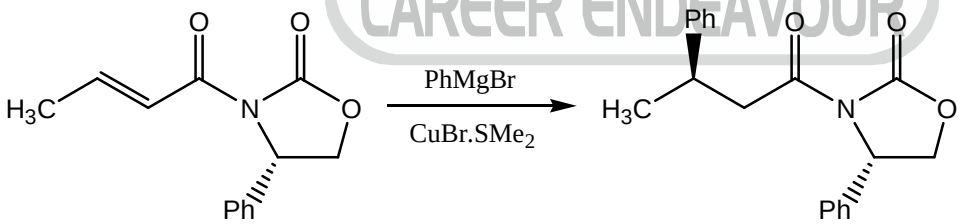



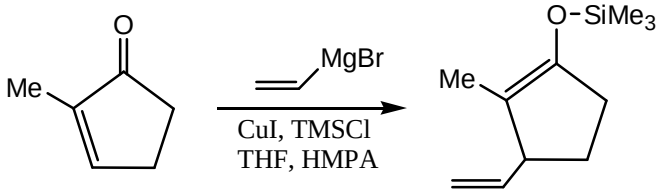

**Remark:** If addition to α,β-unsaturated ketones are carried out in the presence of $Cu_2Br_2$ then only 1, 4-addition takes place.

**Examples:**

1. 


2. 


3. 


4. 


Grignard reagents can give either or both 1, 2 and 1, 4-addition products on reaction with α, β-unsaturated system. The extent of conjugate (1, 4) addition depends mostly on the nature of the substituents attached to the unsaturated carbonyl electrophile. In the absence of significant steric interactions, 1, 2-addition takes place using substrates such as α,β-unsaturated aldehydes or unhindered α, β-unsaturated ketones.