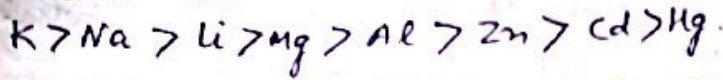
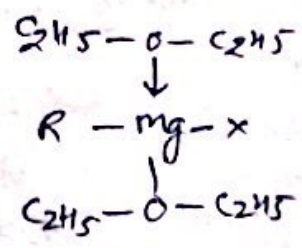


organometallic reagents are versatile compounds of organic synthesis. The ionic character of Carbon-metal bond depends on the nature of the metal as -



It is believed that a Grignard reagent exists as coordination complex with ether.

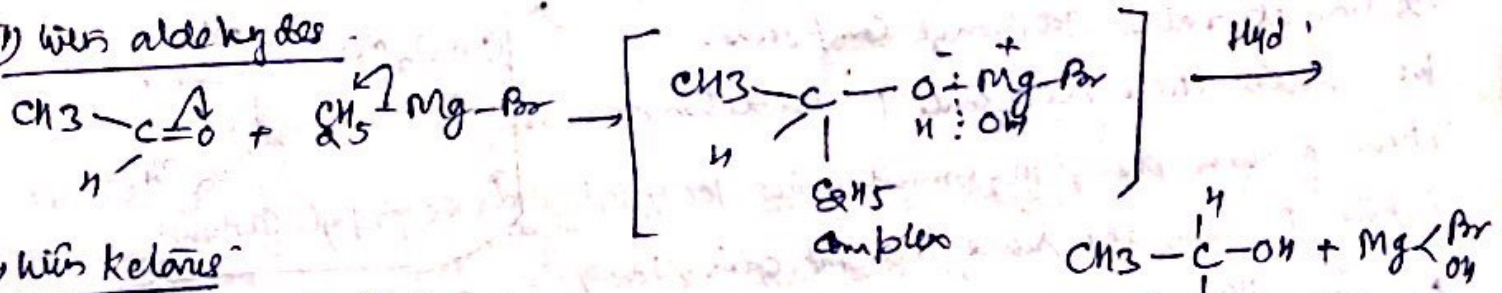


A Grignard reagent may be regarded as polar compound and is a source of nucleophilic carbon ion

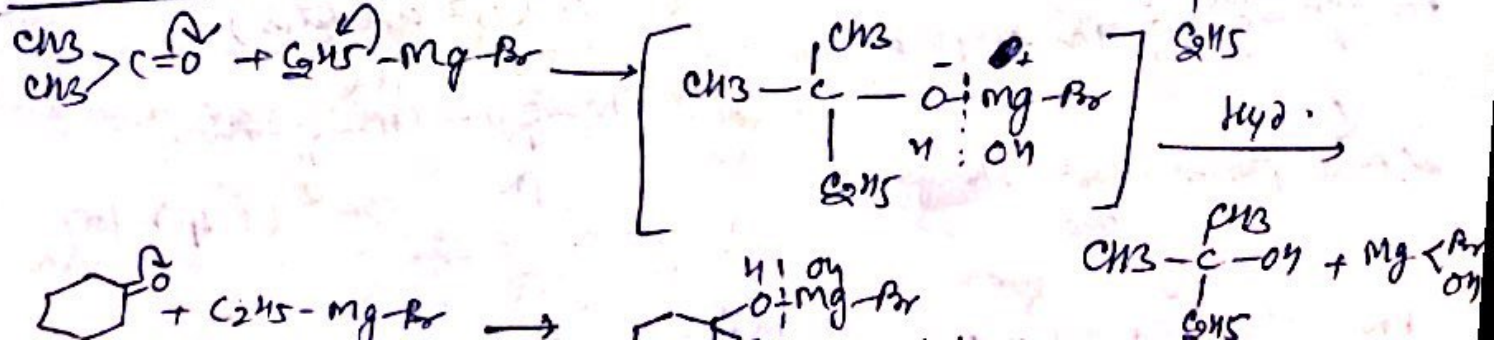
$$R^{\delta-}Mg^{\delta+}-X$$

Reactions with Carbonyl Compounds As we know C-Mg bond will generate nucleophilic carbon, compared to normal bond polarisation of C-Br bond which generates electrophilic carbon ($C^{\delta-}-Mg^{\delta+}$) Thus they function as carbon nucleophile. It is an example of reverse polarisation. The main use of Grignard's reagents is as carbon ions, usually in reactions with carbonyl compounds. They attack carbonyl carbon of the aldehydes, ketones, esters, anhydrides, acid chlorides etc. In this process alkyl group becomes attached to the carbonyl carbon and Mg-halide to the oxygen. to form a complex which is then decomposed with water to form hydroxy compound.

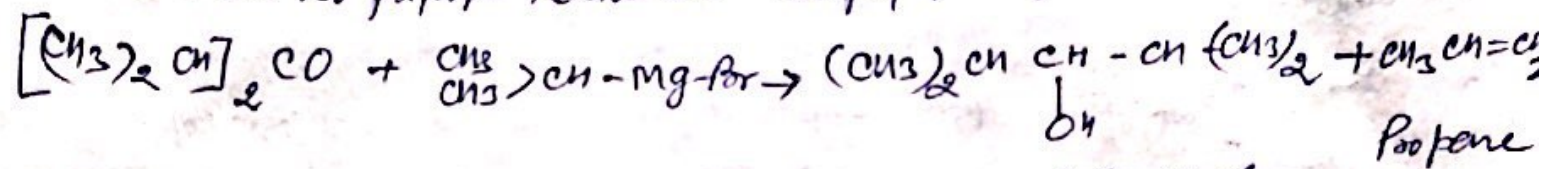
1) with aldehydes



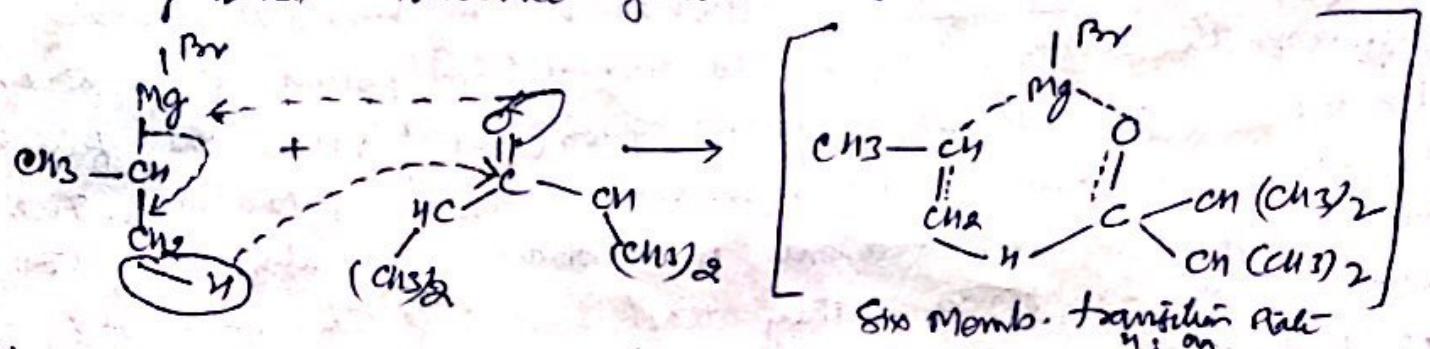
2) with ketones



By arching of the carbon chain near carbonyl group causes steric hindrance. Similarly bulky alkyl or aryl group in Grignard reagent prevents attack of the reagent on electrophilic carbon of the carbonyl compound. There are certain reactions in which substituted ketones and reagents react together to form products which are not obtained in normal Grignard reactions e.g. reaction between di isopropyl ketone and iso propyl Mg bromide



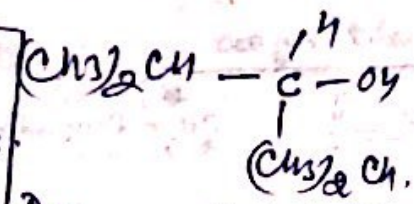
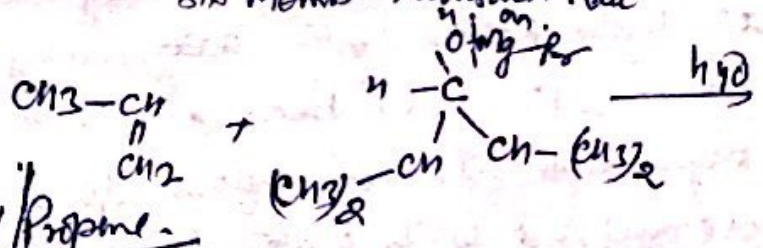
This reaction takes place by hydride transfer from alkyl group of the Grignard reagent involving a six membered cyclic transition state



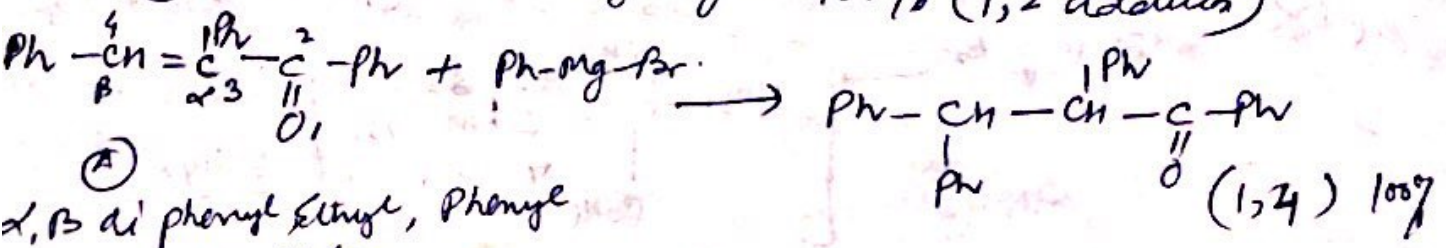
This reaction is quite similar to Meerwein-Ponndorf-Verley rean. of G.R.

Addition to Unsaturated Carbonyl Compds

Grignards reagents also add to unsaturated carbonyl compounds but with these reagents 1,2 addition occurs.



Thus (A) with phenyl Mg bromide gives 100% (1,4) addn while (B) with the same reagent gives 100% (1,2 addition)



(A) α,β di phenyl Ethyl, Phenyl Ketone

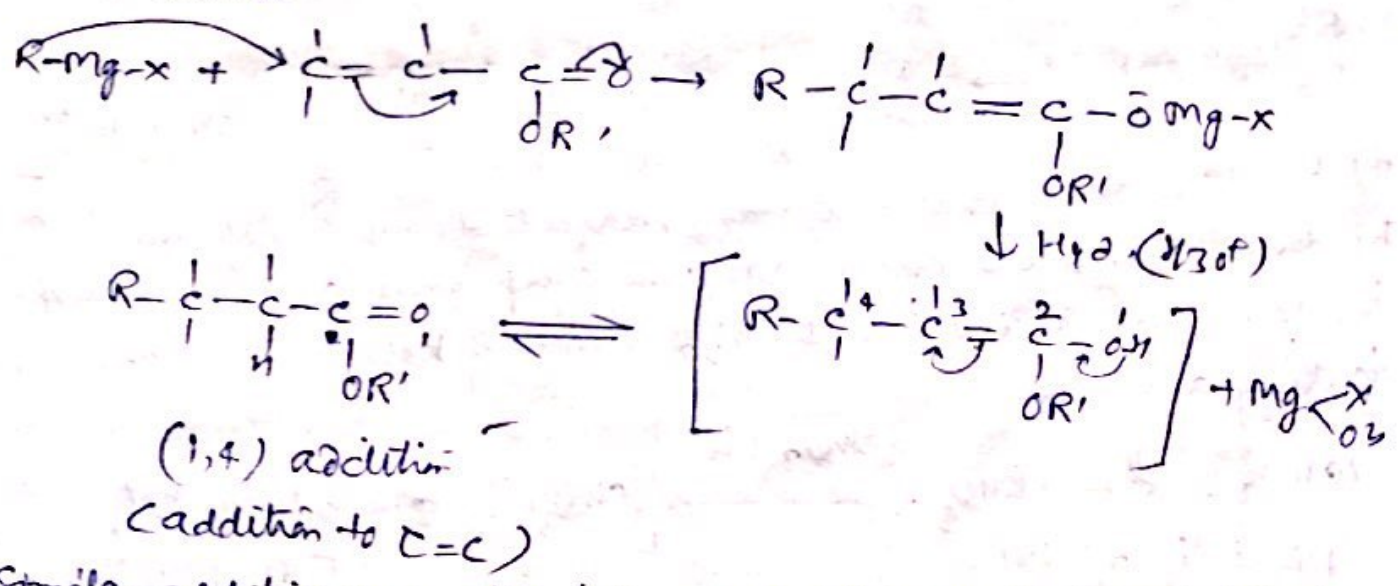
B α 2

In general substitution at the carbonyl group increases 1,4 addition ⁽⁷⁾
 while substitution at the double bond increases 1,2 addition.

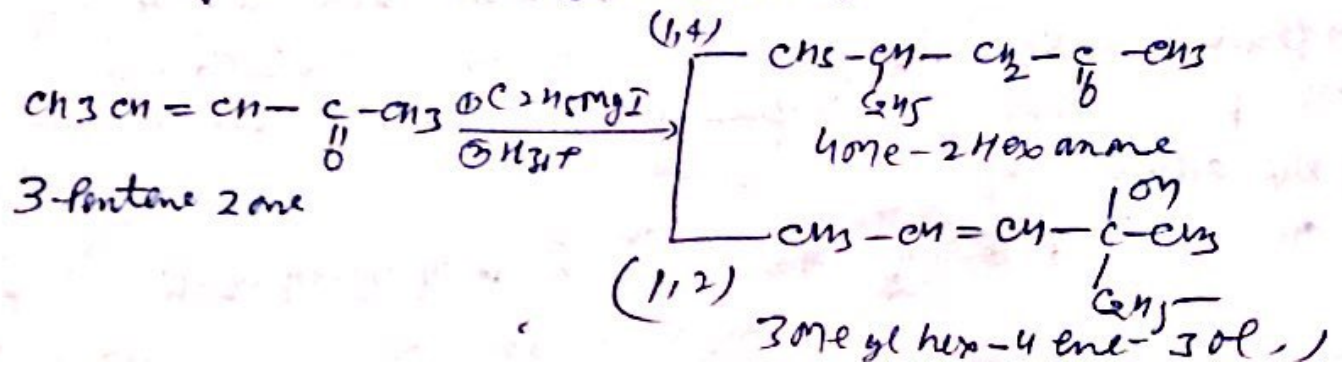
In most cases both products are obtained, but α, β unsaturated aldehydes nearly ^{always} give 1,2 addition when treated with Grignard reagents.
 However, the extent of 1,4 addition of Grignard reagent can be increased by the use of a copper ion catalyst e.g. $\text{CuCl} \cdot 2\text{Cu}(\text{OAc})_2$.

It is likely that alkyl copper reagents formed from RMgX and Cu^+ ion are actual attacking species. Simple alkenes are not attacked by Adding organic lithium compounds to unsatd. carbonyl compds.

nucleophile because there is very little or no electronic polarisation. If $\text{C}=\text{C}$ is polarized by electron withdrawing neighbouring groups then nucleophilic addition to $\text{C}=\text{C}$ is possible. Thus in case of α, β unsaturated esters the addition of Grignard reagents take place as 1,4 addition.

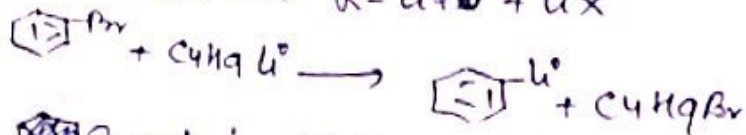
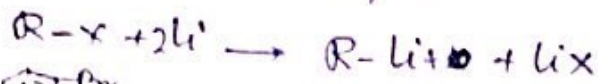


Similar addition may also take place with conjugated aldehydes and ketones. The reaction usually gives a mixture of two products arising from addition to $\text{C}=\text{C}$ double bond (1,4 addition) and carbon-oxygen double bond (1,2 addition)



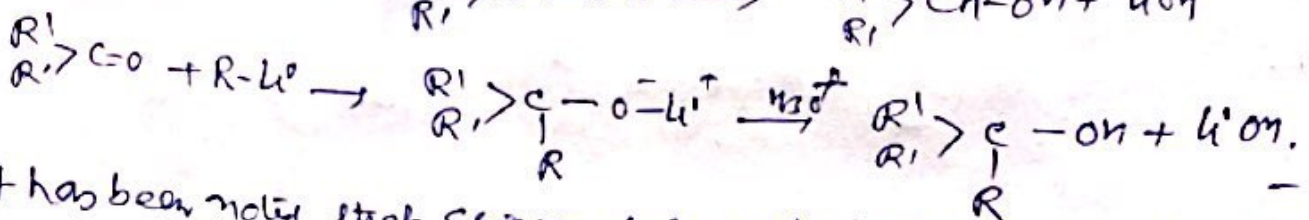
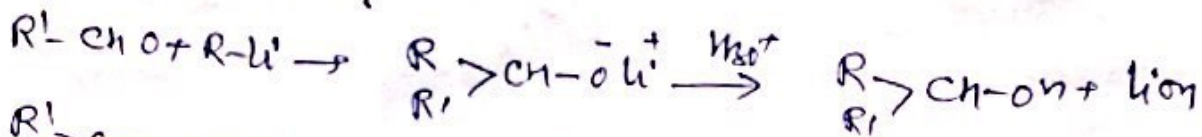
Addition of organo lithium compounds.

These compounds are characterised by C-Li bond and are widely used in organic synthesis. They are more reactive than Grignard reagents. They behave both as nucleophile and a base.

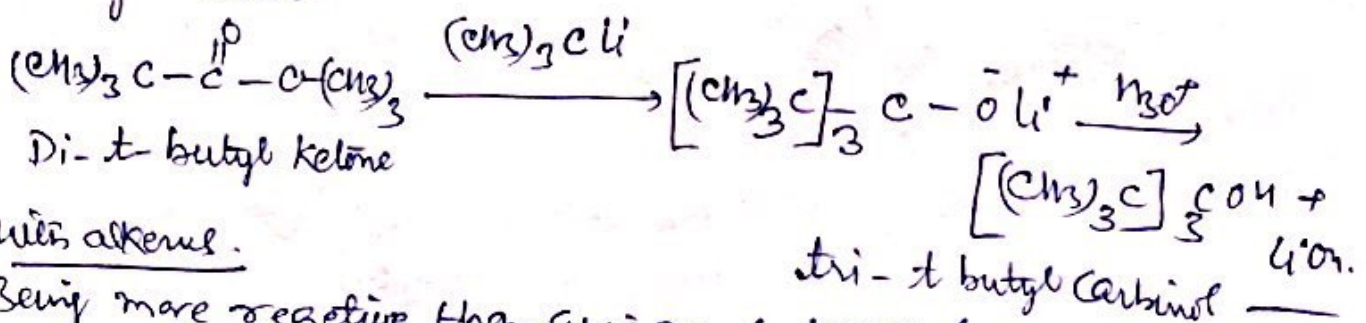


Reactions with Carbonyl Compounds.

Like Grignard reagents, organo lithium reagents react with aldehydes to form secondary alcohols and with ketones to form tertiary alcohols. Yields of alcohols in organo lithium case is better than that of Grignard reagents.



It has been noted that Grignard reagents do not react with hindered ketones while organo lithium compounds are less susceptible to steric factors and react with hindered ketones to form tertiary alcohols.



With alkenes.

Being more reactive than Grignard reagents, they react with alkenes to give alkyl-lithium, which reacts with second molecule of alkene to give corresponding alkyl-lithium.

The process continues depending upon the relative amount of the alkene.

