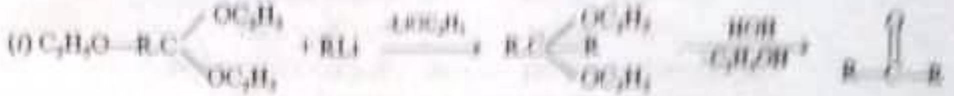
$$(ii)\ H.C{\equiv}N + RLi \longrightarrow \underset{\displaystyle R}{HC}{=}NLi \xrightarrow[-LiOH]{H_2O} RCH{=}NH \xrightarrow{H_2O} RCHO + NH_3$$

5. *Preparation of ketones** : Like aldehydes, ketones are prepared by the reaction between organolithium compounds with any orthoester other than orthoformic ester or alkyl cyanide.



$$(i)\ C_2H_5O{-}R.C\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix} + RLi \xrightarrow{-LiOC_2H_5} R.C\begin{matrix} OC_2H_5 \\ R \\ OC_2H_5 \end{matrix} \xrightarrow[-C_2H_5OH]{HOH} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R$$

$$(ii)\ CH_3C{\equiv}N + RLi \longrightarrow CH_3\underset{\displaystyle R}{C}{=}NLi \xrightarrow[-LiOH]{H_2O} CH_3\underset{\displaystyle R}{C}{=}NH \xrightarrow{H_2O} CH_3\underset{\displaystyle R}{C}{=}O + NH_3$$

Ketones can also be prepared from carbon dioxide (See B type of reactions) or carboxylic acids.

6. *Alkyl cyanides* : These are prepared by the interaction of cyanogen chloride and RLi.

$$RLi + ClCN \longrightarrow RCN + LiCl$$

7. *Preparation of amines* : These are prepared by the reaction between RLi and chloramine as follows.

$$RLi + ClNH_2 \longrightarrow R.NH_2 + LiCl$$

8. *Preparation of thioalcohols* : These are prepared by the action of organolithium compounds on sulphur, and hydrolysing the product.

$$RLi + S \longrightarrow RSLi \xrightarrow{HOH} RSH + LiOH$$

9. *Preparation of alkyl iodides* : By the action of iodine on RLi.

$$RLi + I_2 \longrightarrow RI + LiI$$

10. *Preparation of other organometallic compounds* : Other organometallic compounds can be prepared by the action of metal halide and organolithium compounds as follows.

$$3CH_3Li + AuBr_3 \longrightarrow (CH_3)_3Au + 3LiBr$$
$$2CH_3Li + CdCl_2 \longrightarrow (CH_3)_2Cd + 2LiCl$$
$$4CH_3Li + SiCl_4 \longrightarrow (CH_3)_4Si + 4LiCl$$

Difference from Grignard reagents : As already described organolithium compounds are more reactive than Grignard reagents so the former undergo some additional reactions as well as differ in some of the Grignard reactions, *viz.*

1. *Action on ketones (Preparation of tertiary alcohols)* : Organolithium compounds are very less effected by steric hindrance and thus react normally at carbonyl group to from tertiary alcohols, *e.g.* isopropyl lithium adds successfully on di-isopropyl ketone to from tertiary alcohol.

$$\underset{\text{isopropyl lithium}}{Me_2CHLi} + \underset{\text{Di-isopropyl ketone}}{[Me_2CH]_2CO} \longrightarrow (Me_2CH)_3COLi \xrightarrow{HOH} \underset{\text{Tri-isopropylcarbinol}}{(Me_2CH)_3C{-}OH}$$

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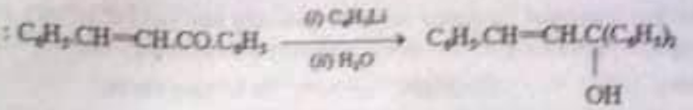
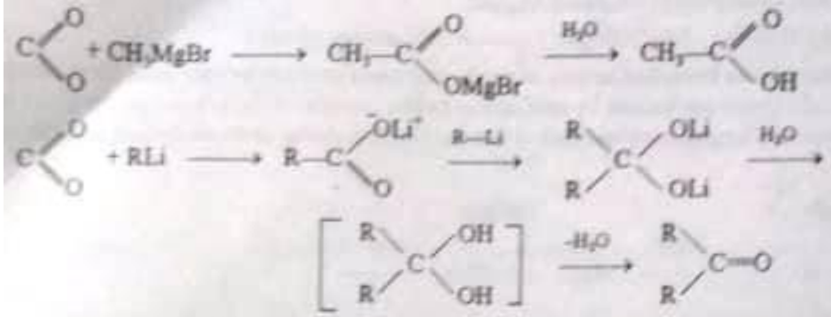
*also difference from Grignard reactions.

1, 2-Addition :



$$C_6H_5CH{=}CH.CO.C_6H_5 \xrightarrow[(ii)\ H_2O]{(i)\ C_6H_5Li} C_6H_5CH{=}CH.\underset{\underset{OH}{|}}{C}(C_6H_5)_2$$

Addition on carbon dioxide (preparation of ketones) : Carbon dioxide gives carboxylic acids with the Grignard reagent but ketones with the organolithium compounds.



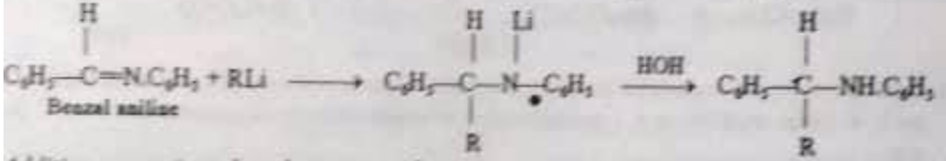
The difference is due to the fact that the organolithium compounds are more strongly nucleophilic than Grignard reagents and hence react with the intermediate resonance stabilized carboxylate anion. Due to this reason carboxylic acids are also used in synthesising ketones from lithium compounds.

Addition on olefinic double bonds : Unlike Grignard reagents, organolithium compounds add on ethylenic double bonds. The addition takes place at high pressure (100–500 atmospheres) on simple olefins, *e.g.*, ethylene.

$$C_6H_5Li + CH_2{=}CH_2 \longrightarrow C_6H_5CH_2{-}CH_2Li \xrightarrow{CH_2=CH_2} C_6H_5(CH_2)_4Li \xrightarrow{CH_2=CH_2} \text{etc.}$$

but at atmospheric pressure on conjugated olefins.

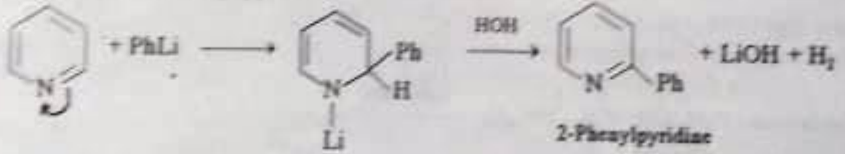
Organolithium compounds also add on $\rangle C{=}NR$ to give amines, *e.g.*



$$C_6H_5{-}\overset{\overset{H}{|}}{C}{=}N.C_6H_5 + RLi \longrightarrow C_6H_5{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{\overset{Li}{|}}{N}{-}C_6H_5 \xrightarrow{HOH} C_6H_5{-}\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}{-}NH.C_6H_5$$

Benzal aniline

Addition on activated carbon atom of aromatic system : Organolithium compounds, unlike Grignard reagents, add on activated carbon atom of the aromatic system which on hydrolysis gives ubstitution products, *e.g.* pyridine.



2-Phenylpyridine

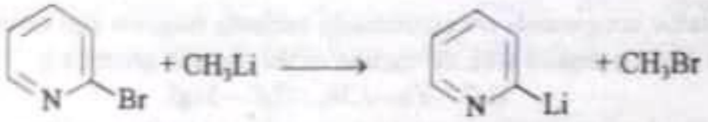
Organocadmium Compounds

admium alkyls and aryls can be obtained by the action of cadmium chloride on a Grignard reagent ganolithium compound

As aryl halides are less prone to Wurtz reaction the aryl lithium compounds can be p
n at the b.pt. of the solvent.

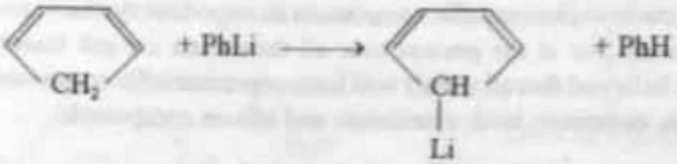
tal halogen exchange : Since aryl and vinyl halides do not react well with metallic lithiu
responding lithium compounds are prepared by the metal-halogen exchange reaction, *e.*

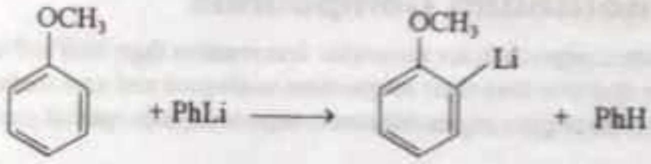
$$C_6H_5Br + \underset{\text{butyl lithium}}{C_4H_9Li} \longrightarrow C_4H_9Br + \underset{\text{phenyl lithium}}{C_6H_5Li}$$



$$CH_2{=}CHBr + C_3H_7Li \longrightarrow CH_2{=}CHLi + C_3H_7B$$

talation by phenyl lithium : The metalation is suitable for the preparation of lithium deriva
nparatively acidic hydrocarbons, *e.g.*





n organomercury compounds : Organolithium compounds can also be conveniently prep
ing the lithium metal with organomercury compound, *e.g.*

$$R_2Hg + 2Li \longrightarrow 2RLi + Hg$$

tions and Uses

ke Grignard reagents, organolithium compounds can be used to synthesise most of the ty
ompounds. Organolithium compounds resemble very much with organomagnesium comp
cal properties except few differences. So the chemical reactions of organolithium compoun
d under two headings : **(a)** those in which they resemble with Grignard reagents and **(b)** th
ey differ from Grignard reagents.

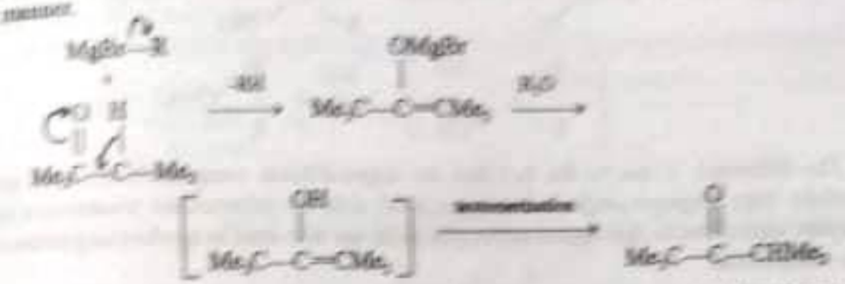
On the other hand, Grignard reagents give very low yield of tertiary alcohols with ketones containing bulky group, e.g. di-t-butylketone does not form tertiary alcohols with Grignard reagents.

$(Me_3C)_2CO$ + $CH_3MgBr \longrightarrow$ No tertiary alcohol

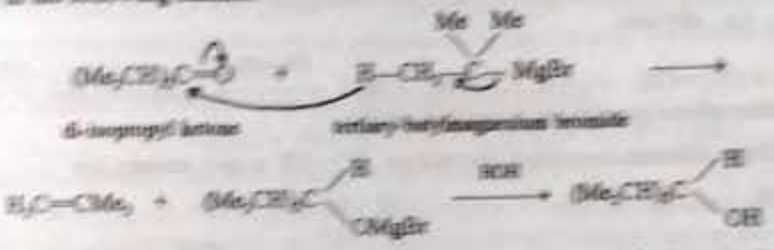
Moreover, if the Grignard reagent contains a branched alkyl group and the ketone contains somewhat less bulky groups, yields are again low, viz. di-isopropyl ketone fails to give tertiary alcohols with isopropyl and tertiary-butyl Grignard reagents.

$(Me_2CH)_2CO$ + $Me_2CHMgBr \longrightarrow$ No tertiary alcohol

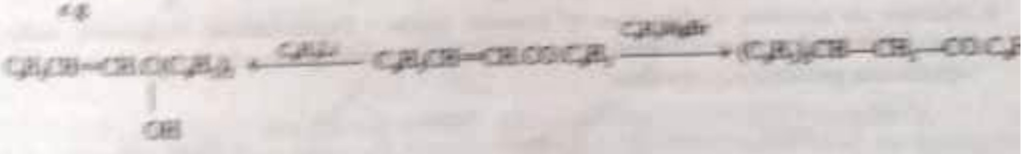
In these cases instead of tertiary alcohols, enols and/or secondary alcohols (depending upon the nature of ketone) are formed by enolization and/or reaction of the ketonic group. If the ketone has at least one hydrogen atom on either of its two α-carbon atoms, enols are formed in the following manner.



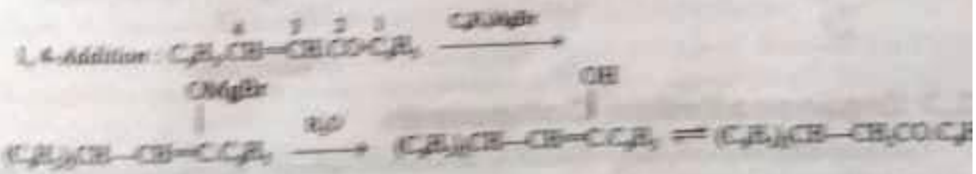
If the Grignard reagent contains at least one hydrogen atom on its β-carbon atom reduction occurs in the following manner.



2. *Addition on α, β-unsaturated ketones*: Grignard reagents add on α, β-unsaturated ketones either on 1, 4- (main product) or 1, 2-position whereas organolithium compounds add on 1, 2-position e.g.



$$C_6H_5CH{=}CH\underset{\displaystyle OH}{\underset{|}{C}}(C_6H_5)_2 \xleftarrow{C_6H_5Li} C_6H_5CH{=}CHCOC_6H_5 \xrightarrow{C_6H_5MgBr} (C_6H_5)_2CH{-}CH_2{-}COC_6H$$



1, 4-Addition : $C_6H_5\overset{4}{C}H{=}\overset{3}{C}H\overset{2}{C}O{-}\overset{1}{C}_6H_5 \xrightarrow{C_6H_5MgBr}$

$$(C_6H_5)_2CH{-}CH{=}\overset{\displaystyle OMgBr}{\overset{|}{C}}C_6H_5 \xrightarrow{H_2O} (C_6H_5)_2CH{-}CH{=}\overset{\displaystyle OH}{\overset{|}{C}}C_6H_5 \rightleftharpoons (C_6H_5)_2CH{-}CH_2CO{\cdot}C_6H$$

(A) **Resemblance with Grignard reagents.** Organolithium compounds give most of the reactions of organomagnesium compounds ; some of which are given below.

1. *Preparation of hydrocarbons* : Like Grignard reagents they react with compounds containing active hydrogen to give corresponding hydrocarbon, viz

$$RLi + HOH \longrightarrow R{-}H + LiOH$$

$$RLi + R'OH \longrightarrow R{-}H + LiOR'$$

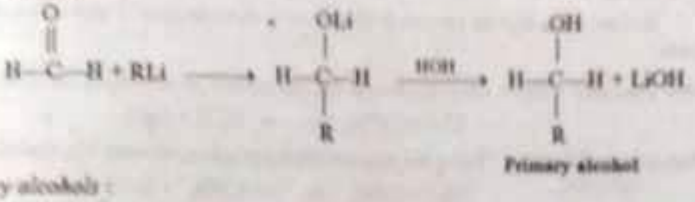
$$RLi + BrCH_3 \longrightarrow R{-}CH_3 + LiBr$$

$$CH_3CH{=}CHLi + R'OH \longrightarrow CH_3CH{=}CH_2 + LiOR'$$

$$CH{\equiv}CLi + R'OH \longrightarrow CH{\equiv}CH + LiOR'$$

2. *Preparation of alcohols* : Primary, secondary and tertiary alcohols can be prepared by the action of organolithium compounds on formaldehyde, CH_3CHO and ketone, respectively.

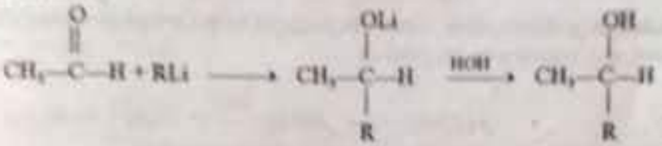
(a) *Primary alcohols* :



$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + RLi \longrightarrow H{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OLi}{|}}{C}}{-}H \xrightarrow{HOH} H{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}H + LiOH$$

Primary alcohol

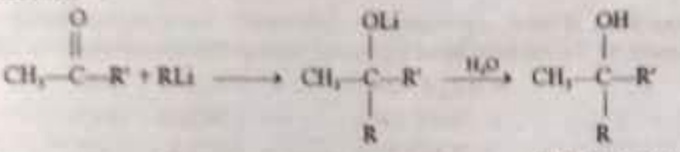
(b) *Secondary alcohols* :



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + RLi \longrightarrow CH_3{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OLi}{|}}{C}}{-}H \xrightarrow{HOH} CH_3{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}H$$

Secondary alcohol

(c) *Tertiary alcohols** :



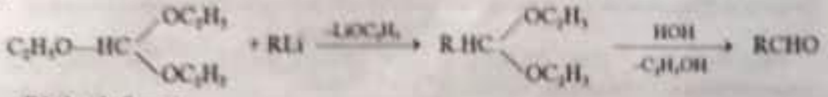
$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R' + RLi \longrightarrow CH_3{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OLi}{|}}{C}}{-}R' \xrightarrow{H_2O} CH_3{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}R'$$

Tertiary alcohol

3. *Preparation of ethers* : Higher ethers are prepared by the action of organolithium compounds on a monochloroether.

$$ROCH_2Cl + R'Li \longrightarrow ROCH_2R' + LiCl$$

4. *Preparation of aldehydes* : Aldehydes are prepared by the reaction between organolithium compound with ethyl orthoformate or hydrogen cyanide.

(i) 

$$C_2H_5O{-}HC\begin{matrix}\diagup OC_2H_5\\ \diagdown OC_2H_5\end{matrix} + RLi \xrightarrow{-LiOC_2H_5} R.HC\begin{matrix}\diagup OC_2H_5\\ \diagdown OC_2H_5\end{matrix} \xrightarrow[-C_2H_5OH]{HOH} RCHO$$

Ethyl orthoformate

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* See also difference from Grignard reactions