

Dear students! Thank you all a lot for the feedback that you have given for the last article. This is the last part of Organometallic Compounds. Hopefully, this will fulfil the requirement of COMPETITIVE EXAMINATIONS you are going to face. Moreover, some more problems will be given in upcoming issues. Do read the basics of every chapter very carefully. Do take care, all the best!

\*Arunava Sarkar

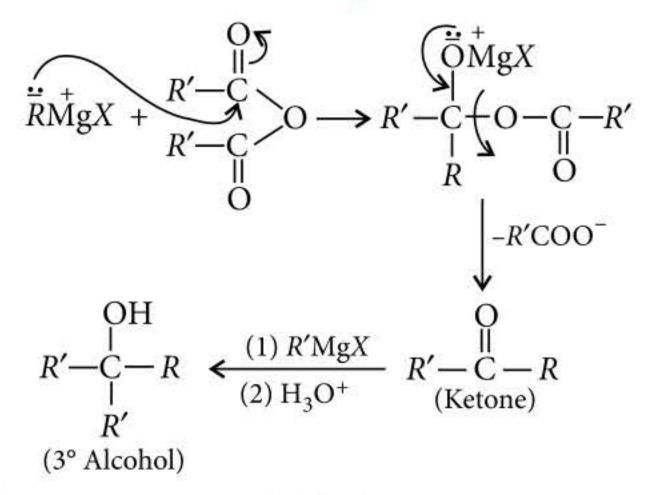
## A BRIEF OVERVIEW OF ORGANOMETALLIC REAGENTS AND ORGANOMETALLIC CHEMISTRY

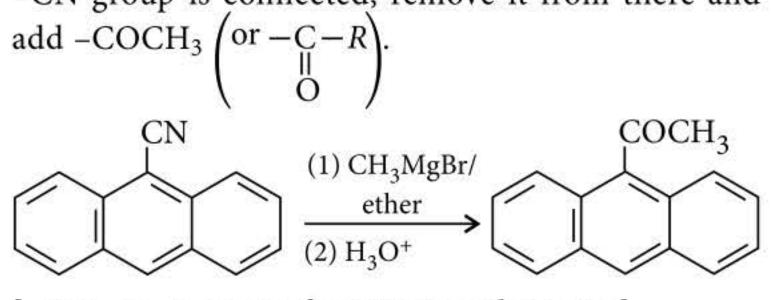
## **GRIGNARD REAGENTS**

## **O** Reaction with nitriles

Remember the basic idea here which is, whereever -CN group is connected, remove it from there and

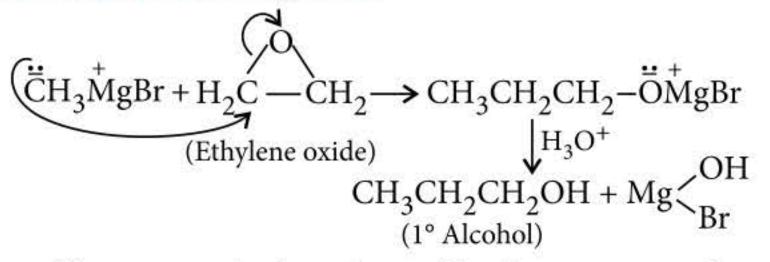
## **O** Reaction with acid anhydride



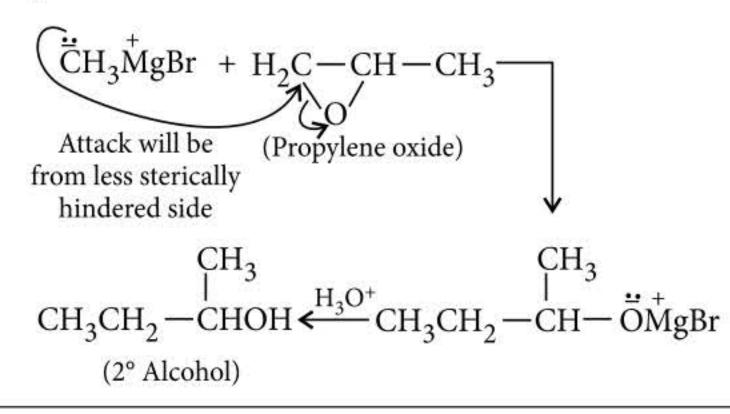


 $[-CH_3 \text{ or } -R \text{ comes from Grignard reagent}]$ 

**O** Reaction with epoxide



If you use substituted epoxide, then you can also get 2° alcohol.



## **O** Reaction with alkyl halide

Reaction between Grignard reagent and an alkyl halide is often carried out very slowly as Grignard reagent is prepared from alkyl halide. So, the reaction between Grignard reagent and alkyl halide is carried out in presence of transition metal catalyst, specifically cobalt chloride (CoCl<sub>2</sub>). This kind of transition metal catalysed reaction is known as Kharasch reaction. For example,

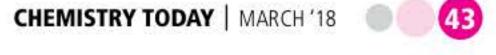
$$CH_{3}MgBr + CH_{3}CH_{2}Br \xrightarrow{CoCl_{2}} CH_{3}CH_{2}CH_{3}$$
(\approx 68\%-70\%)

It has been found that a reaction is possible in between Grignard reagent and  $\alpha$ -haloketone. For example,

$$C_6H_5COCH_2Cl + C_6H_5MgBr \xrightarrow{(1) dry ether, -28 °C}{(2) ice cold HCl}$$
  
 $C_6H_5COCH_2C_6H_5$ 

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## **ORGANOLITHIUM COMPOUNDS**

Obviously, organolithium compounds are characterised by a C – Li bond. Li is less electronegative than carbon and hence, the polarisation of carbon-lithium bond is shown as below :

$$\geq^{\delta = -\delta_{+}}_{C-Li}$$

Organolithium compounds are more reactive than Grignard reagents, however the nature of reaction remains the same in most of the cases and in some cases distinctly different.

## Preparation of organolithium compounds

From alkyl or aryl halides

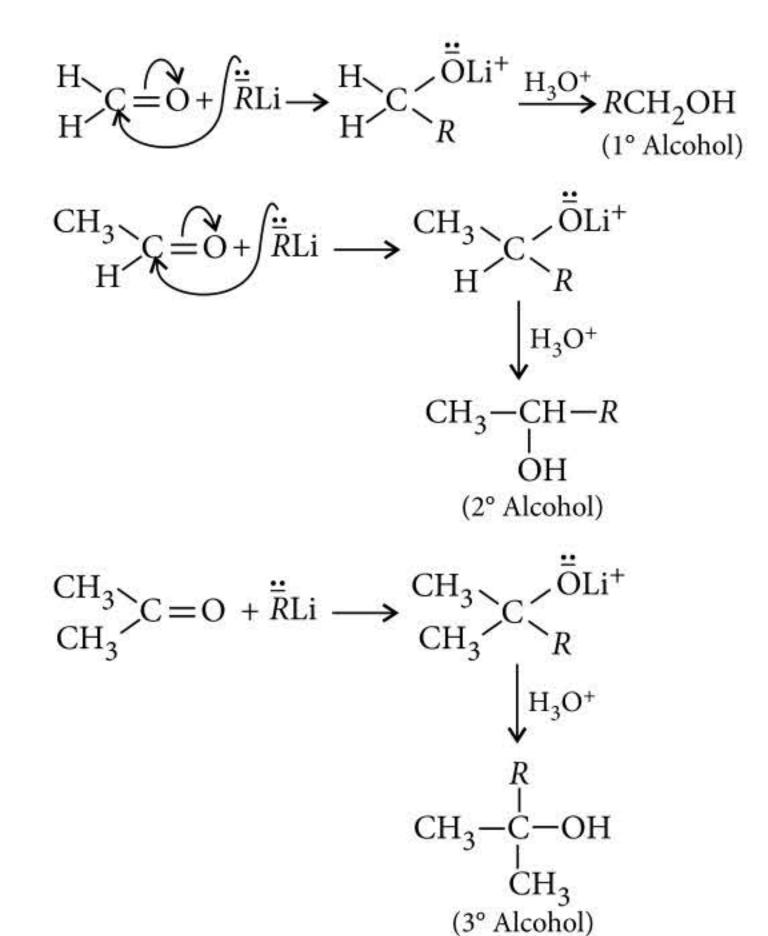
$$R - X + 2Li$$
  $\xrightarrow{\text{low temperature}}$   $R - Li + LiX$   
inert atmosphere (Ar)

Order of reactivity : R - I > R - Br > R - Cl

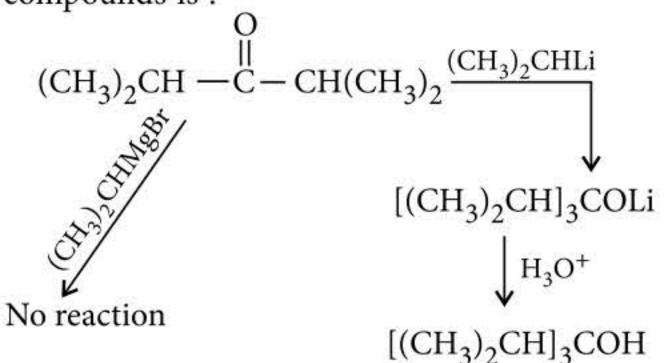
## Halogen-metal exchange

$$R - X + R' \text{Li} \longrightarrow R - \text{Li} + R' - X$$
  
e.g.,

$$\bigcirc \operatorname{Br}_{+ n-C_4H_9Li} \longrightarrow \bigcirc \operatorname{Li}_{+ n-C_4H_9Br}$$



An important reaction to show the difference in reactivity between Grignard reagent and organolithium compound before getting into discussion on the reactions shown by organolithium compounds is :



So, organolithium compounds are more reactive than organomagnesium compounds.

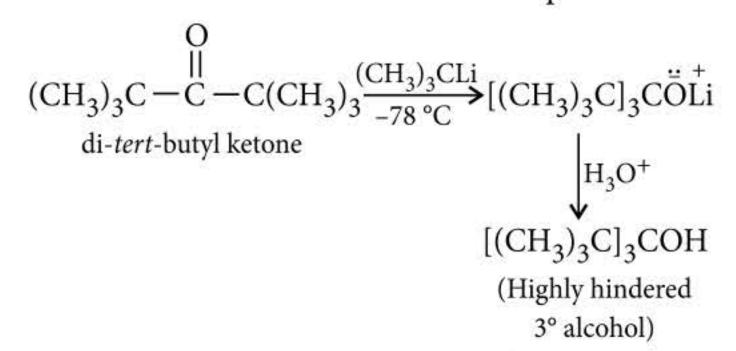
## Most useful reactions of organolithium compounds

Reaction with carbonyl compounds (with the focus on conjugated carbonyl compounds)

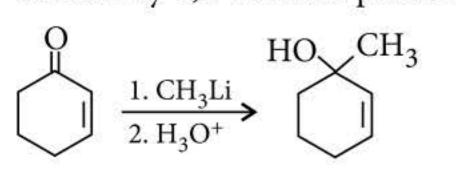
Let us start the discussion with the similarities in the reactions with Grignard reagent.

Grignard reagent reacts with formaldehyde to give 1° alcohol (after hydrolysis), acetaldehyde to give 2° alcohol (after hydrolysis), acetone to give 3° alcohol (after hydrolysis). Same goes with organolithium compounds.

For the third case, there is a well known advantage of using organolithium compounds over Grignard reagents that is Grignard reagents do not react with hindered ketones but organolithium compounds do. Here is the best and most used example :



Now, let us take the case of  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds. We have seen that with  $\alpha$ ,  $\beta$ -unsaturated compounds, Grignard reagent can give either 1,2-addition or 1,4-addition product depending on the overall steric hindrance whereas organolithium compounds on the other hand, give exclusively 1,2-addition products.



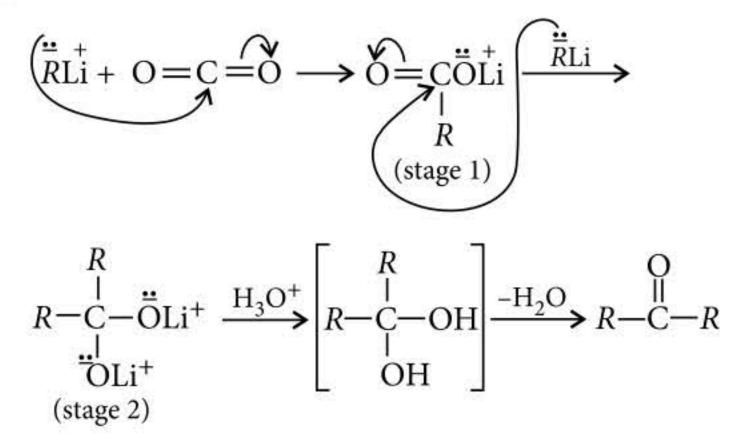
[The reason for this is that organolithium compounds are aggressive nucleophiles.]





However, lithium dialkyl cuprates give exclusively 1,4-addition product.

Reaction with carbon dioxide 0

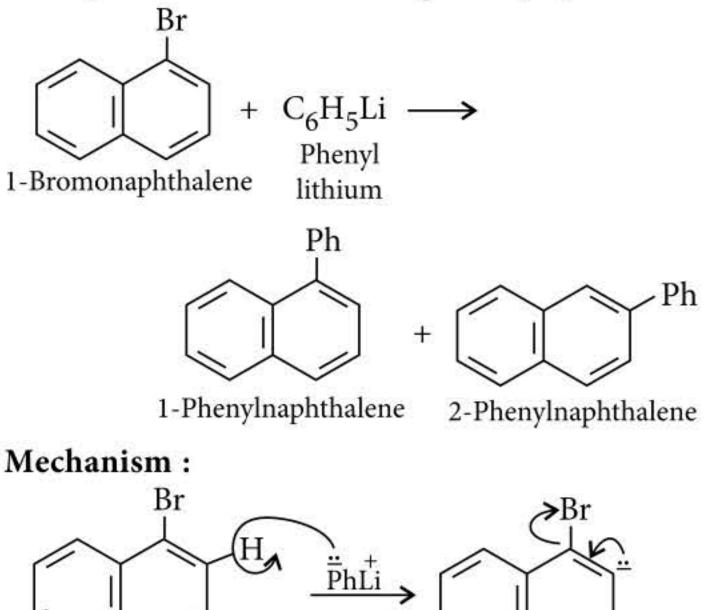


So, here is an important difference with the Grignard reagent. In case of Grignard reagent, the reaction stops at stage 1 i.e., 1 mole addition of Grignard reagent but in case of organolithium compounds, the reaction goes upto stage 2 i.e., 2 moles addition of organolithium compound.

Electrophilic displacement

$$R \xrightarrow{f} X + \int \frac{1}{R'} Li^+ \xrightarrow{S_N^2} R - R' + LiX$$

It is to be remembered that in case of substitution in aromatic rings, elimination-addition reaction takes place. Take the following example,



 $R - X + R' Li \longrightarrow RLi + R' - X$ 

A specific example of this kind can be given :

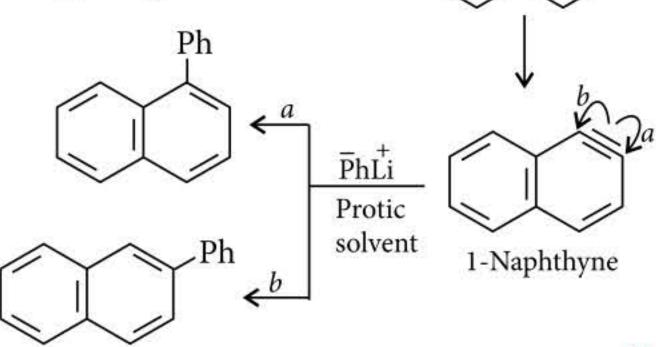
 $CH_2 = CHBr + nC_4H_9Li \longrightarrow$ 

Vinyl bromide n-Butyl lithium

 $CH_2 = CHLi + nC_4H_9Br$ 

## Nucleophilic displacement 0

Here, a similar reaction as happens in Wurtz reaction takes place.



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