# CONCEPT BOOSTER

Hello students ! After the massive winter season how we all are waiting for the upcoming SEASON OF EXAMS hopefully our favourite season. Anyway this article is dedicated to a specific and one of the most wanted topics "ORGANOMETALLIC COMPOUNDS & THEIR REACTIONS". I have found you all are having so many doubts with the use of organometallic compounds. Hopefully this article will help you intensively. Keep practicing all my dear students & enjoy your study.

*Arunava Sarkar

A BRIEF OVERVIEW OF ORGANOMETALLIC REAGENTS AND ORGANOMETALLIC CHEMISTRY

Organometallic reactions are those where the metals act as catalysts. The most important thing is transition metal complexes and reagents can make impossible reactions occur easily. Take the following example at the beginning :
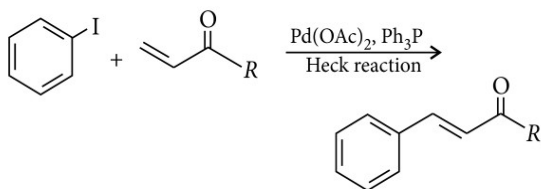

What you can see is Heck reaction couples an alkene with an organic halide or triflate to form a new alkene. Triflates are trifluoromethanesulphonate anions, conveniently denoted as $CF_3SO_3^-$ or TfO^-.

Triflates are non-basic very good leaving groups. We can say that triflates are oxygen based leaving groups and even better than halides. The basic funda is metals are inserted between $-\overset{|}{\underset{|}{C}}-OSO_2CF_3$ bond. Triflates are usually prepared conveniently with Comin's reagent :
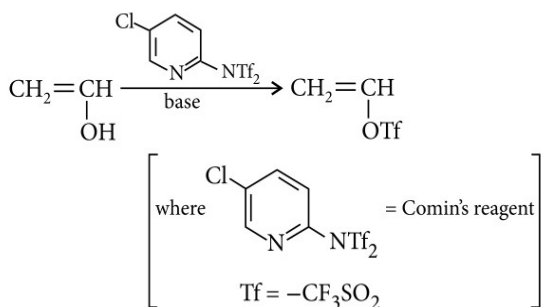
In general, the simple outline of the Heck reaction can be shown below :

$$R-X + R'-CH=CH-H \xrightarrow[\text{base}]{\text{Pd(0) catalyst}}$$
$$R-CH=CH-R' + H-X$$
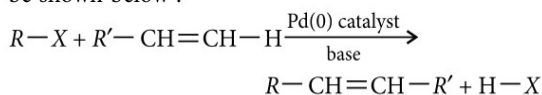
In general, whenever we say organometallic compounds, the first thing which comes to our mind is Grignard reagent. We'll have a quick look on the important parts of Grignard reagent :

$$R-X + Mg \xrightarrow[\text{reflux}]{\text{dry ether}} R-MgX$$
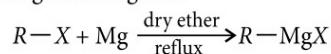
For a given halogen, the reactivity order of alkyl groups is $-CH_3 > -C_2H_5 > -C_3H_7$ and for a given alkyl group, the reactivity order of halogens is $RI > RBr > RCl$.

As the reactions of Grignard reagent are concerned, the most important one is reaction with carbonyl compounds. This is actually nucleophilic addition reaction. Here, an important point should be understood. Normally, if you take $-\overset{|}{\underset{|}{C}}-X$ (X being the halogen) then the polarity is $-\overset{|}{\underset{|}{\overset{\delta+}{C}}}-\overset{\delta-}{X}$. But, if you take Grignard reagent, then the polarity is as shown below :

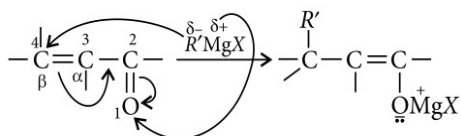$$-\overset{|}{\underset{|}{\overset{\delta-}{C}}}-\overset{\delta+}{MgX}$$
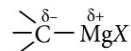
So, there is a polarity reversal. This is known as **umpolung**. So, Grignard reagent gives carbanion. Reaction between a carbonyl group and Grignard reagent takes place as shown below :
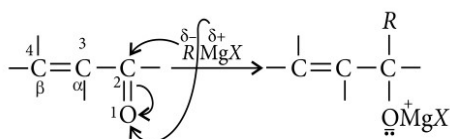

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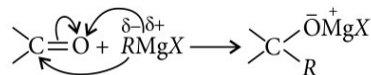
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Now, if we consider a carbon-carbon multiple bond system only, then Grignard reagent doesn't attack there. But, if the carbon-carbon multiple bond is in conjugation with carbon-oxygen double bond then the addition of Grignard reagent takes place and this is popularly known as Michael addition. Here, we have two possibilities of addition. One is 1,4-addition and the another one is 1,2-addition. Let me show you nature of both the additions :
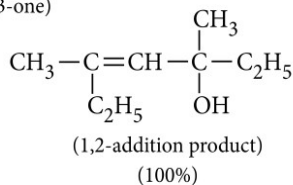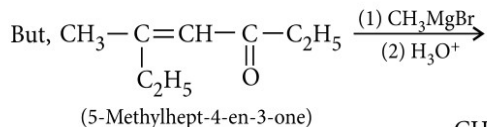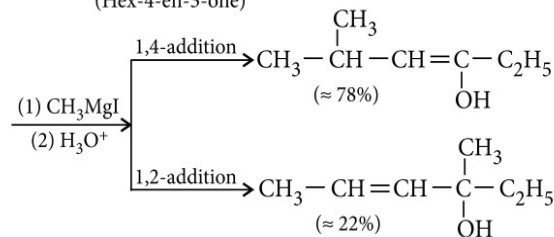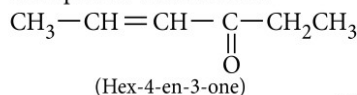
1,4-addition :

$$-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}-\overset{R'}{\underset{\overset{|}{\underset{1}{O}}}{}} \xrightarrow{\overset{\delta-\ \delta+}{R'MgX}} -\overset{R'}{\underset{}{C}}-C=C-$$

1,2-addition :

$$-\overset{4}{C}=\overset{3}{C}-\overset{2}{C}-\overset{}{\underset{\overset{|}{\underset{1}{O}}}{}} \xrightarrow{\overset{\delta-\ \delta+}{R MgX}} -C=C-\overset{R}{\underset{OMgX}{|}}-$$
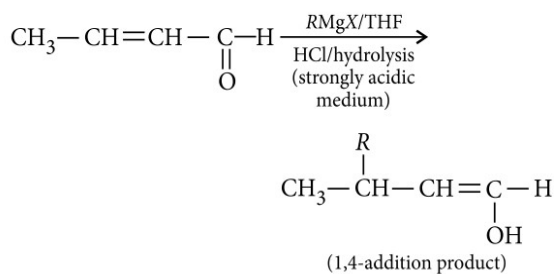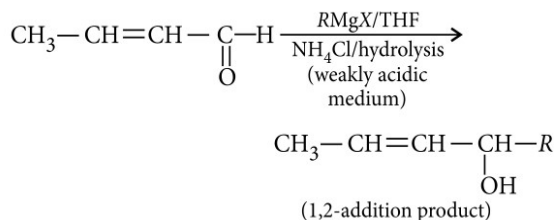
Normally, addition of Grignard reagent is 1,4-addition. But, if the β-carbon is crowded, then exclusively 1,2-addition takes place. We can take the following examples to understand :

$$CH_3-CH=CH-\underset{\overset{||}{O}}{C}-CH_2CH_3$$
(Hex-4-en-3-one)

$$\xrightarrow[\text{(2) } H_3O^+]{\text{(1) } CH_3MgI}$$

1,4-addition → $CH_3-\underset{}{CH}-CH=\underset{\overset{|}{OH}}{C}-C_2H_5$ (with CH_3) (≈ 78%)

1,2-addition → $CH_3-CH=CH-\underset{\overset{|}{OH}}{C}-C_2H_5$ (with CH_3) (≈ 22%)

But, $CH_3-\underset{\overset{|}{C_2H_5}}{C}=CH-\underset{\overset{||}{O}}{C}-C_2H_5 \xrightarrow[\text{(2) } H_3O^+]{\text{(1) } CH_3MgBr}$
(5-Methylhept-4-en-3-one)

$$CH_3-\underset{\overset{|}{C_2H_5}}{C}=CH-\underset{\overset{|}{OH}}{\overset{CH_3}{C}}-C_2H_5$$
(1,2-addition product)
(100%)

It is also important to note that nature of reaction of Grignard reagent depends also on the supporting reagent. For example :

$$CH_3-CH=CH-\underset{\overset{||}{O}}{C}-H \xrightarrow[\substack{NH_4Cl/hydrolysis \\ \text{(weakly acidic} \\ \text{medium)}}]{RMgX/THF}$$

$$CH_3-CH=CH-\underset{\overset{|}{OH}}{CH}-R$$
(1,2-addition product)

$$CH_3-CH=CH-\underset{\overset{||}{O}}{C}-H \xrightarrow[\substack{HCl/hydrolysis \\ \text{(strongly acidic} \\ \text{medium)}}]{RMgX/THF}$$

$$CH_3-\underset{\overset{|}{R}}{CH}-CH=\underset{\overset{|}{OH}}{C}-H$$
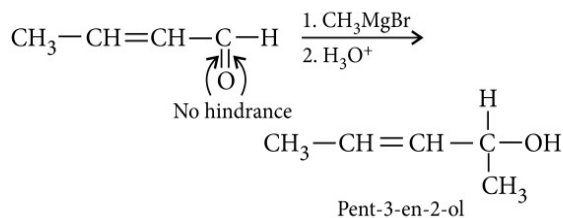(1,4-addition product)

So, we can see that a strong atmosphere (medium) supports 1,4-addition whereas a weak atmosphere supports 1,2-addition.

Now, there is another aspect which gives another concept. In case of α,β-unsaturated aldehyde (like crotonaldehyde) where there is no hindrance at the $\overset{}{C}=O$ group, there the major product is unsaturated alcohol via 1,2-addition.
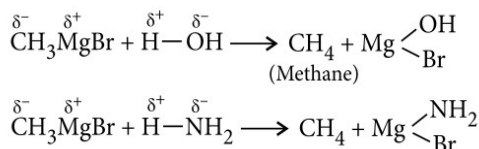
$$CH_3-CH=CH-\underset{\underset{(O)}{\|}}{C}-H \xrightarrow[\text{2. } H_3O^+]{\text{1. } CH_3MgBr}$$

No hindrance

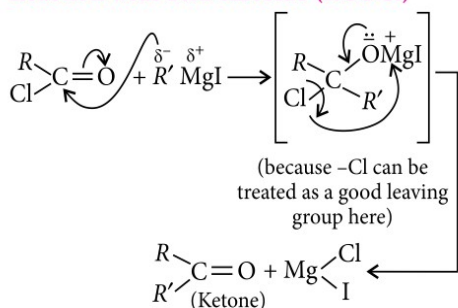$$CH_3-CH=CH-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OH$$

Pent-3-en-2-ol

Now, we can take a look into the different reactions exhibited by Grignard reagent.

○ **Reaction with compounds containing active hydrogen**

$$\overset{\delta^-}{C}H_3\overset{\delta^+}{Mg}Br + \overset{\delta^+}{H}-\overset{\delta^-}{O}H \longrightarrow CH_4 + Mg\overset{OH}{<}_{Br}$$
(Methane)

$$\overset{\delta^-}{C}H_3\overset{\delta^+}{Mg}Br + \overset{\delta^+}{H}-\overset{\delta^-}{N}H_2 \longrightarrow CH_4 + Mg\overset{NH_2}{<}_{Br}$$

Similar reactions are obtained with 1° amines, alcohols, etc. containing active hydrogen. Look at a fact that if you fix the alkyl group of Grignard reagent as methyl, then everytime methane is the product. Now, if we take a known amount of the compound containing active hydrogen then by measuring the amount of methane liberated, we can find out the number of active hydrogens present in the compound. This is known as Zerewitinoff determination.
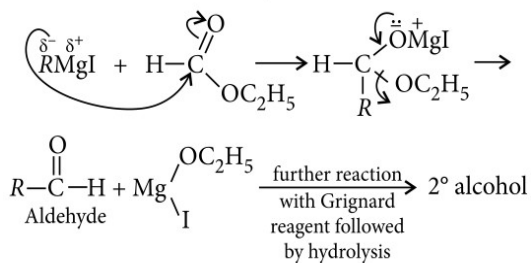
○ **Reaction with acid chloride (RCOCl)**

(because –Cl can be treated as a good leaving group here)

$$\underset{R'}{\overset{R}{>}}C=O + Mg\overset{Cl}{<}_{I}$$
(Ketone)

Now, if excess amount of Grignard reagent is present then after hydrolysis 3° alcohol is produced.

$$\underset{R''}{\overset{R}{>}}C\overset{\ddot{O}MgI}{<}_{R'} \text{ , } \underset{R''}{\overset{R}{>}}C\overset{OH}{<}_{R'} \xleftarrow{H_3O^+}$$
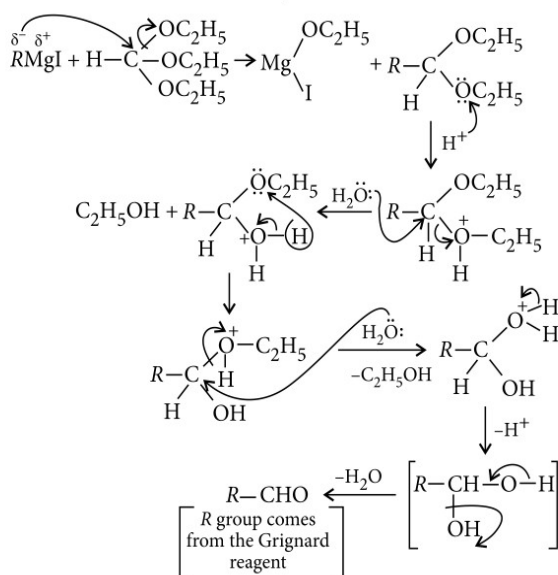(3° alcohol)
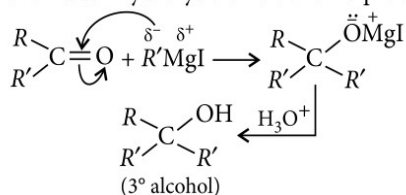
○ **Reaction with ester :** In this case, a diversified range of ester is found. We will take three major examples of esters to display the varieties of reaction of Grignard reagent.
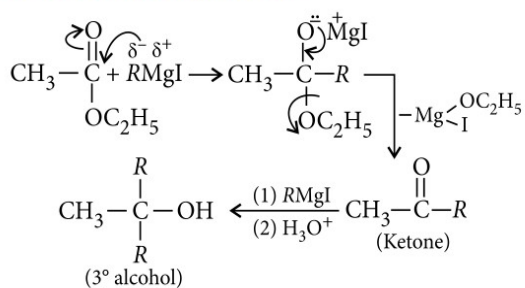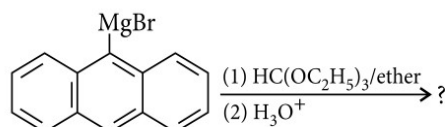
(a) Reaction with ethyl formate

$$\overset{\delta^-}{R}\overset{\delta^+}{Mg}I + H-\overset{\overset{O}{\|}}{C}-OC_2H_5 \longrightarrow H-\underset{\underset{R}{|}}{\overset{\overset{\ddot{O}MgI}{+}}{C}}-OC_2H_5 \longrightarrow$$

$$\underset{\text{Aldehyde}}{R-\overset{\overset{O}{\|}}{C}-H} + Mg\overset{OC_2H_5}{<}_{I} \xrightarrow[\substack{\text{with Grignard} \\ \text{reagent followed} \\ \text{by hydrolysis}}]{\text{further reaction}} \text{2° alcohol}$$

(b) Reaction with ethyl *ortho*-formate

$$RMgI + H-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}-OC_2H_5 \rightarrow Mg\overset{OC_2H_5}{<}_{I} + R-\underset{\underset{H}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}-\ddot{O}C_2H_5$$

$$\downarrow H^+$$

$$C_2H_5OH + R-\underset{\underset{+\overset{|}{O}-\overset{|}{H}}{\underset{H}{\underset{|}{}}}}{\overset{\overset{\ddot{O}C_2H_5}{|}}{C}} \xleftarrow{H_2\ddot{O}:} R-\underset{\underset{H}{|}}{\overset{\overset{OC_2H_5}{|}}{C}}\overset{+}{\ddot{O}}-C_2H_5$$

$$\downarrow$$

$$R-\underset{\underset{OH}{}}{\overset{\overset{+}{O}-C_2H_5}{C}}H \xrightarrow[-C_2H_5OH]{H_2\ddot{O}:} R-\underset{\underset{OH}{}}{\overset{\overset{+}{O}-H}{C}}H$$

$$\downarrow -H^+$$

$$\underset{\substack{R \text{ group comes} \\ \text{from the Grignard} \\ \text{reagent}}}{R-CHO} \xleftarrow{-H_2O} \left[R-\underset{\underset{OH}{|}}{\overset{\overset{O-H}{|}}{CH}} \right]$$

○ **Reaction with ethyl acetate**

$$CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{O}{\|}}{C}} + RMgI \rightarrow CH_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{\ddot{O}MgI}{+}}{C}}-R \overset{-Mg\overset{OC_2H_5}{<}_{I}}{\longrightarrow}$$

$$\underset{(3° \text{ alcohol})}{CH_3-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH} \xleftarrow[\text{(2) } H_3O^+]{\text{(1) } RMgI} \underset{(Ketone)}{CH_3-\overset{\overset{O}{\|}}{C}-R}$$

Q. Identify the product.

$$\xrightarrow[\text{(2) } H_3O^+]{\text{(1) } HC(OC_2H_5)_3/\text{ether}} ?$$
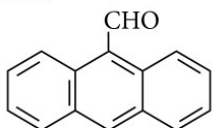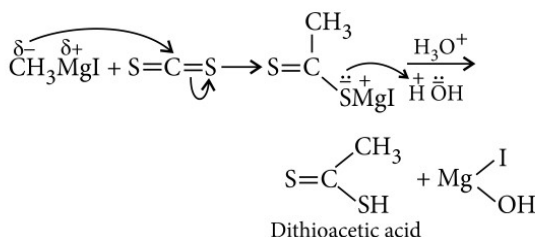
Soln.: Idea is very simple. Concept of using *ortho*-formate is, wherever –MgBr is attached, just add –CHO

there. So, the product is

○ **Reaction with carbon disulphide**
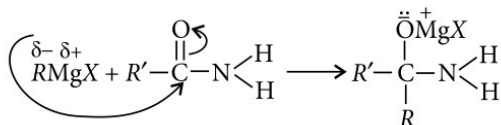

Dithioacetic acid

○ **Reaction with carbon dioxide**

Ethanoic acid
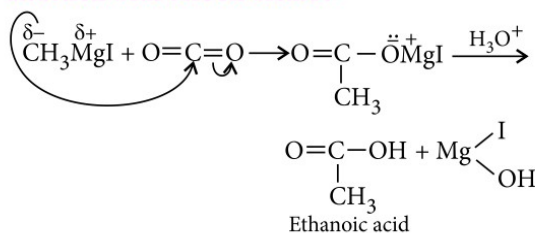
○ **Reaction with acid amide**
The first member of amide is formamide

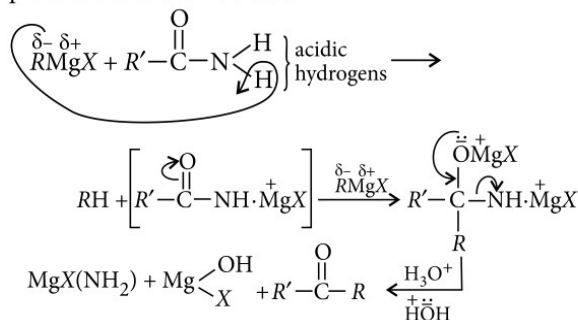$$\left(H-\overset{\overset{O}{\parallel}}{C}-N\overset{H}{\underset{H}{\diagdown}} \right).$$ When Grignard reagent reacts with

formamide, it gives aldehyde whereas with other amides, Grignard reagent gives ketone.
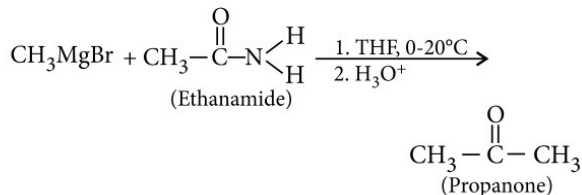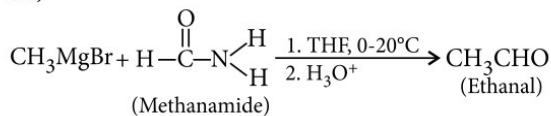In general, the reaction proceeds as shown below :
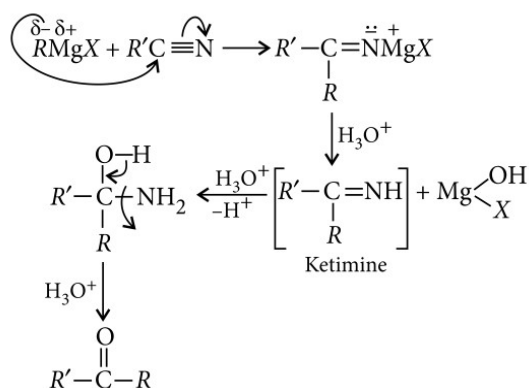

Look carefully!!
This is not the way the reaction proceeds. The reaction proceeds as shown below :

So,

(Methanamide)   (Ethanal)

(Ethanamide)

$$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_3$$
(Propanone)

○ **Reaction with nitriles**

Ketimine

$$R'-\overset{\overset{O}{\parallel}}{C}-R$$