Some inorganic reagent and their application in Organic Reaction:

There are many reagent required for the proposed synthesis of organic compound, chemists may required to perform several types of reaction like oxidation, reduction, selective reduction, ozonolysis, methylation acetoxylation etc.

To perform there type of synthesis a chemist may need to use such specific reagent. These reagents are also used in structural determination of unknown compound (organic). Few of these reagents are

(a) $LiAlH_4$ (Lithium aluminium hydride) (b) $NaNH_2$ (Sodamide) (c) $NaBH_4$ (Sodium borohydride)

(d) SeO_2 (selenium dioxide) etc.

(1) $LiAlH_4$ (Lithium aluminium hydride)

This is useful and powerful reducing agent ~~reaction~~ which was first discovered by Finholt and co-worker in 1947.

Preparation - It is prepared by adding gradually a calculated quantity of aluminium chloride, to a thin paste of lithium hydride in presence of ether.

$$4\,LiH + AlCl_3 \xrightarrow[\text{ether}]{} LiAlH_4 + 3LiCl$$

Lithium aluminium hydride

Application of $LiAlH_4$:- $LiAlH_4$ is a

Function of dry ether: Universal reducing agent, as many reductions, which are considered to be impossible, made possible by use of this reagent due to following merits

(I) It requires mild reaction condition
(II) It reduces a large variety of organic compound like aldehyde, ketone, acid ester epoxides etc.
(III) It is selective reducing agent for reducing aldehyde group of unsaturated hydrocarbon without affecting double bond, however when phenyl group is attached to β-carbon of α-β unsaturated carbonyl compd (group), the double bond is also attacked.
(IV) One molecule of $LiAlH_4$ can reduce four molecules of aldehydes or ketones.
Structure of Grignard reagent
(V) After use it can be easily destroyed by adding ethyl acetate.

Reduction of aldehydes, ketones, acid and acid derivatives:

(i) $CH_3-CH_2-CH=O$ (1 mole) $\xrightarrow[(0.25\ mole)]{LiAlH_4}$ $CH_3-CH_2-CH_2-OH$. 1-propanol.

(ii) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + LiAlH_4 \rightarrow CH_3-\underset{OH}{\underset{|}{CH}}-CH_3$ 2-Butanol.

(iii) $CH_3-(CH_2)_{16}-COOH \xrightarrow{LiAlH_4} CH_3-(CH_2)_{16}-CH_2-OH$

Stearic acid — 1-Octadecanol

(iv) $R-CH(NH_2)COOH \xrightarrow{LiAlH_4} R-CH(NH_2)CH_2OH$

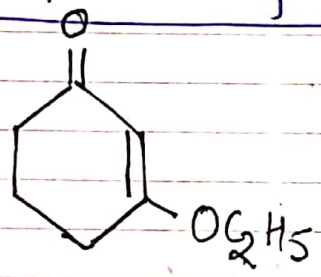
α-amino acid — α-amino alcohol.

(v) $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} R-CH_2-NH_2$

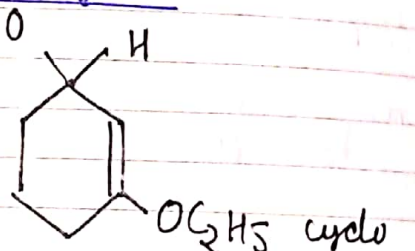
Amide — Primary amine.

(B) Reduction of cyclic ketones, unsaturated aldehyde, acid and nitro compd.

Properties of Grignard reagent.

(i) 

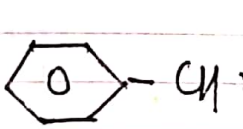
$\xrightarrow{LiAlH_4}$

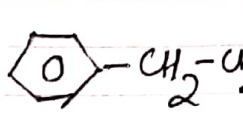


3-ethoxy 2-cyclohexenone — 3-Ethoxy 2-cyclo hexanol

(ii) $CH_3-\overset{\beta}{CH}=\overset{\alpha}{CH}-CHO \xrightarrow{LiAlH_4} CH_3-CH=CH-CH_2-OH$

2-butenal — 2-butenol

(iii) 

$-CH=CH-CHO \longrightarrow$ 

$-CH_2-CH_2-CH_2-OH$

Cinnamaldehyde — dihydro cinnamyl alcohol

However in this case, selective reduction can be done at low temp (−10°C) in ether medium for a short reaction time.

$C_6H_5-CH=CH-CHO \xrightarrow[-10^\circ C,\ ether]{LiAlH_4} C_6H_5-CH=CH-CH_2-OH$

Cinnamaldehyde. Cinnamyl alcohol

(iv) $CH_3-CH=CH-COOH \xrightarrow{LiAlH_4} CH_3-CH=CH-CH_2-OH$

2-butenoic acid 2-buten-1-ol.

(v) $R-C\equiv N \xrightarrow{LiAlH_4} R-CH_2-NH_2$

Nitrile compd. Primary amine.

(c) Reduction of oxime, epoxides, ozonides, halides and sulphur compound.

(i) $R_2C=NOH \xrightarrow{LiAlH_4} R_2-CHNH_2$

oxime primary amine.

(ii) $R-CH-CH_2$ (epoxide) $\xrightarrow{LiAlH_4} R-CH_2-CH_2-OH + R-CH(OH)-$

Primary alcohol

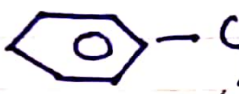
(iii) $R-CH=CH-R' + O_3 \longrightarrow R-CH(O)-CH(O)-R'$ (ozonide)

$R'-CH_2-OH + R-CH_2-OH$ ($\xleftarrow{LiAlH_4}$)

primary alcohol.

(iv) $R-X + LiAlH_4 \longrightarrow RH + LiX + AlX_3$

Alkane



Benzyl bromide.

Toluene.

(v) $R-SO_2Cl + LiAlH_4 \longrightarrow RSH$

Sulphonyl chloride

Thiol.

(D) Estimation of active hydrogen :- It liberates hydrogen gas from an organic compd containing active hydrogen, therefore it is also used in quantitative estimation of hydrogen.

$4\,R\ddot{N}H_2 + LiAlH_4 \longrightarrow [R(\ddot{N}H)_4\overset{\ominus}{Al}]Li^{\oplus} + 4H_2\uparrow$

$4\,R-OH + LiAlH_4 \longrightarrow [(RO)_4\overset{\oplus}{Al}]Li^{+} + 4H_2\uparrow$

complex.

—x— x —x—