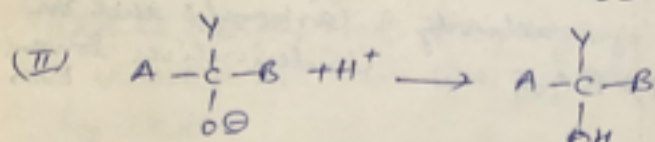
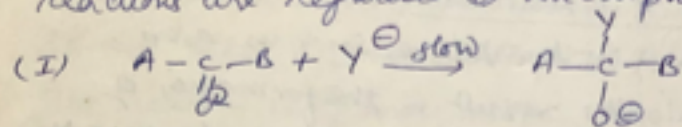


Addition to Carbon-Hetero-multiple bonds.

(1)  
(PIS)

These reactions involve addition to C=O, C=N and C=S double bonds and C≡N triple bond. Since C=O, C=N and C≡N bonds are strongly polar with the carbon always the positive end, there is never any doubt about orientation of unsymmetrical addition to these bonds. Nucleophiles always go to the carbon while electrophilic attacking species go to oxygen or nitrogen. Free radical addition to carbon-hetero bonds are rare. In most of the cases nucleophile attacks first and these reactions are regarded as nucleophilic additions.



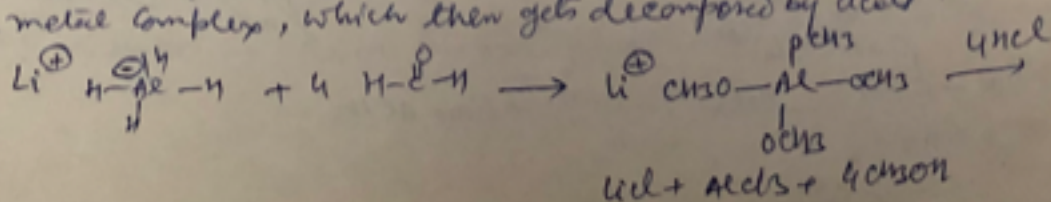
When A and B are H, R or Ar the substrate is an aldehyde or ketone and they almost never <sup>under</sup> go substitution, due to the extremely poor nature of H, R and Ar as leaving group. For acids and their derivatives (B=OH, OR, NR<sub>2</sub>) addition is seldom found, because these are much better leaving groups.

Reaction with hydride donors.

Many reactions of aldehydes and ketones involve transfer of hydride ion H<sup>-</sup> from donor molecule to carbonyl carbon. The common hydride donors are - lithium aluminium hydride, Sodium Borohydride and Aluminium alkoxides, while in Cannizzaro's reaction hydride ion transfer occurs from an already attacked aldehyde molecule.

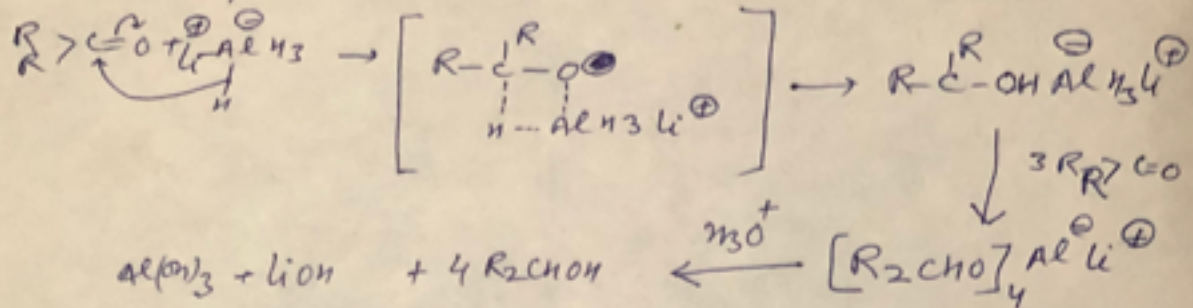
① Lithium Aluminium Hydride LiAlH<sub>4</sub>

It is a reagent widely used for reduction of carbonyl compound to alcohols. All the four hydrogen atoms are available to the carbonyl compound as hydride ion, thus converting it into a metal complex, which then gets decomposed by acids.



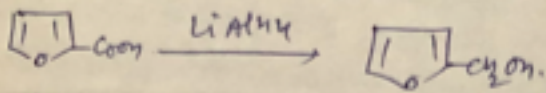
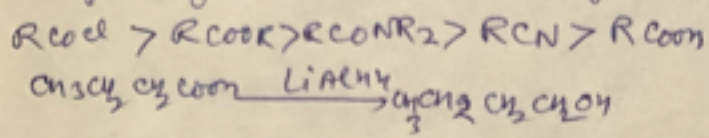


The reaction appears to be a concerted process in which the hydride ion attacks carbonyl carbon and simultaneously the carbonyl oxygen starts complexing with aluminium ion

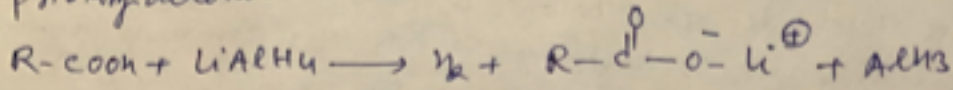


Reduction of Carboxylic acids and its derivative.

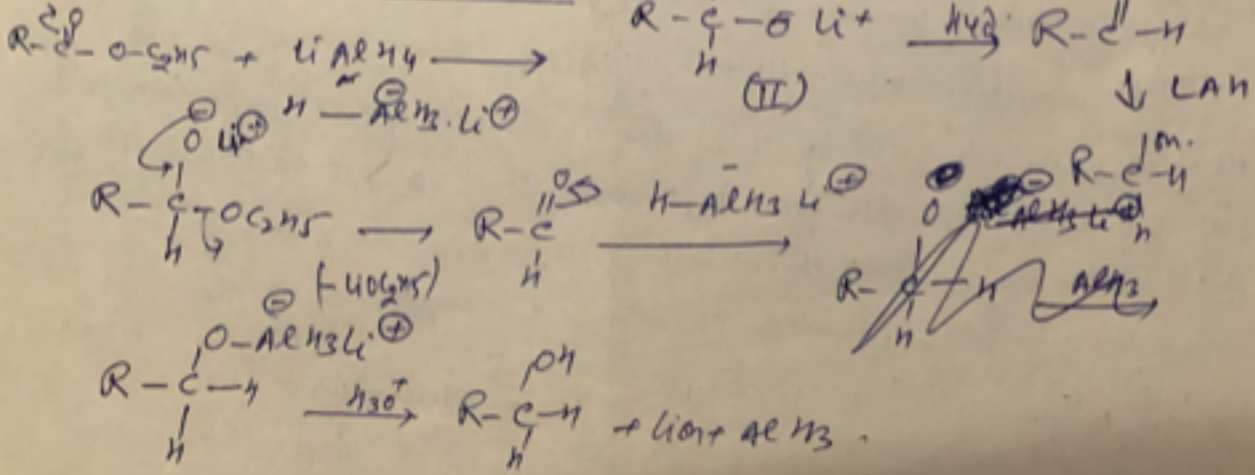
Reduction of carboxylic acids and its derivatives, such as esters, acid anhydrides and acid chlorides result in the formation of corresponding alcohols. The order of reactivity of carboxylic acid and its derivatives toward LAH is



Carboxylic acid reacts with LAH to form carboxylate anion (I) and  $\text{H}_2$ . This is followed by the addition of hydride ion to the carbonyl group to give tetrahedral intermediate (II), which is further reduced to primary alcohol.

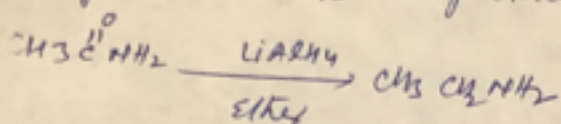


Similarly esters can be reduced

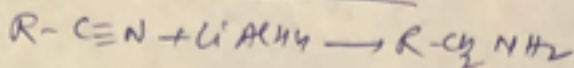




Unsubstituted amides give primary amines, whereas N-sub amide <sup>(3)</sup> give secondary amines and N-N disubstituted amide give tertiary amines.  
 Reduction of amide with LAH gives iminium ion, which is more electrophilic than starting amide so it gets reduced to amine.

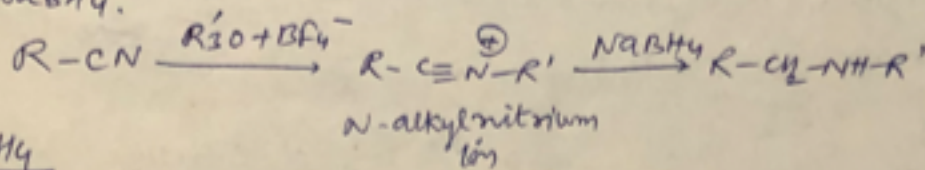


Reduction of nitriles to amines.



$\text{NaBH}_4$  does not generally reduce nitriles but does so in alcoholic solvents when a  $\text{CoCl}_2$  catalyst is added or in presence of Raney Ni. The reaction is of wide scope, it is not possible to stop with the addition of only 1 mole of hydrogen.

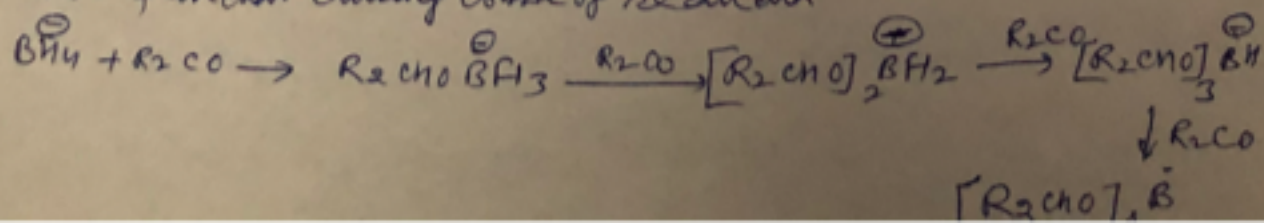
N-alkyl nitrium ions are reduced to secondary amines by  $\text{NaBH}_4$ .



### ③ $\text{NaBH}_4$

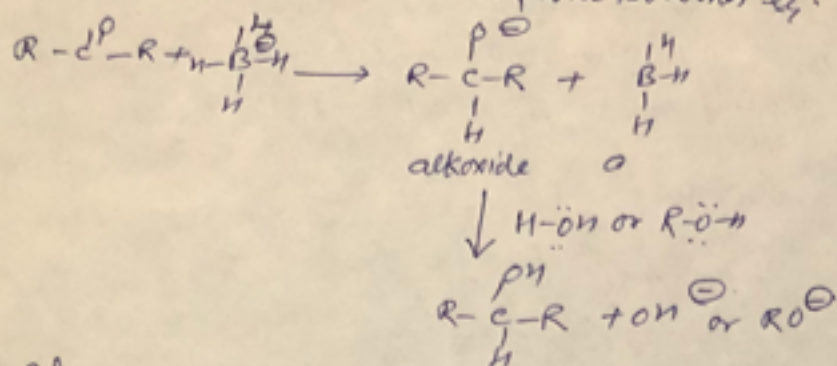
$\text{NaBH}_4$  is a mild reducing agent, which reacts rapidly with aldehydes and ketones but only slowly with esters. Neither  $\text{NaBH}_4$  nor  $\text{LiAlH}_4$  react with isolated  $\text{C}=\text{C}$  double bond. The alkali metal hydrides such as  $\text{NaH}$  are unsuitable reducing agents because of their insolubility in organic solvents and their powerful effect as catalyst for base catalysed condensation.

The most commonly used reagent for reduction of aldehydes and ketones is sodium borohydride  $\text{NaBH}_4$ . Since  $\text{BH}_4^-$  contains four hydride ions it is capable of reducing four molecules of aldehyde or ketone. Reaction proceeds by successive transfer of hydride ion from the boron to four different carbonyl carbons. As all the four hydrides are transferred there are actually several reducing species which function during course of reduction.

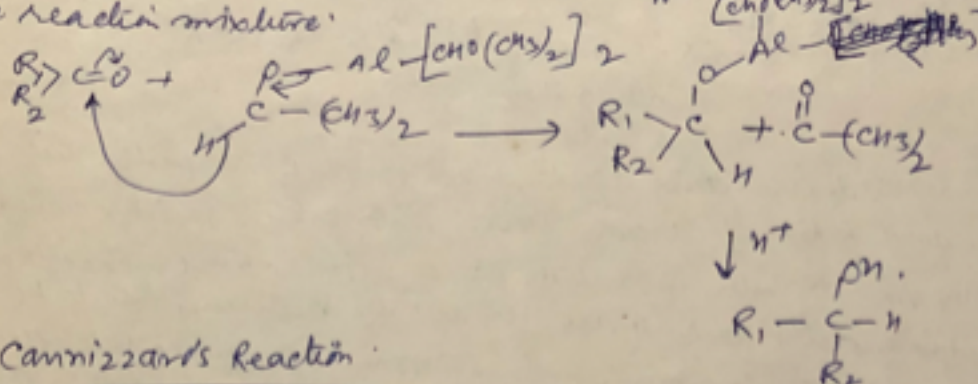




Reduction is carried out either in alcohol or in water. While reductions with LiAlH<sub>4</sub> are done in aprotic solvents, e.g., anhyd. ether.



③ Aluminium alkoxides. This reaction involves the transfer of hydride ions from the metal salts of primary and secondary alcohols to the carbonyl carbon. The reduction of carbonyl compounds to alcohols with Aluminium isopropoxide is very important reaction known as Meerwein-Ponndorf-Verley reduction. Isopropanol is used as the solvent. acetone is distilled off as soon as it is formed from the reaction mixture.



④ Cannizzaro's reaction

Aldehydes which do not have  $\alpha$ -hydrogen atoms cannot undergo base-catalysed condensation, they react with bases by disproportionation involving the transfer of hydride ions. It is self oxidation-reduction reaction. Crossed Cannizzaro's reaction between one molecule of such aldehyde and another molecule of formaldehyde leads to reduction of the former and the oxidation of the latter.

