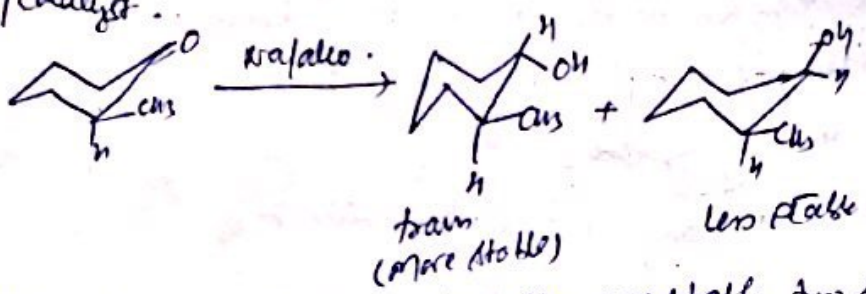


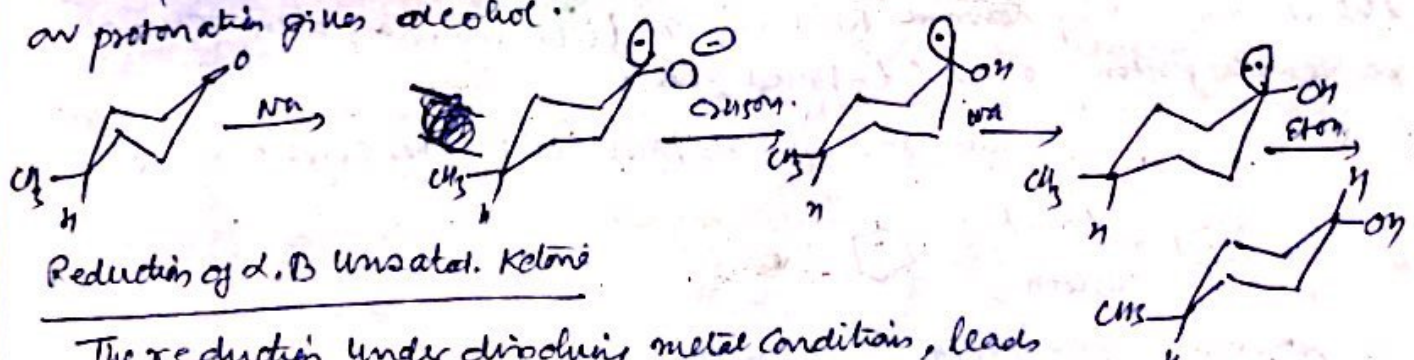
Ketones can be reduced to secondary alcohols by following methods-

- ① By catalytic hydrogenation
- ② With complex hydride
- ③ via reduction by dissolving metal

When cyclic ketones are reduced by Na/alco., the exclusive formation of thermodynamically stable alcohol takes place e.g. on reducing 2-methyl cyclohexanone on reduction with Na/alco gives the more stable trans alcohol in 99% yield. the percentage of trans alcohol decreases sharply on reduction with LiAlH<sub>4</sub> (82%), NaBH<sub>4</sub> (69%) and T-3 % when reduced with Pt/catalyst.



Although no mech is universally acceptable, two suggestions are generally given. According to Barton and Robinson (1957) a tetrahedral diamine is formed initially, which adopts equatorial configuration with oxygen and this on protonation gives alcohol.

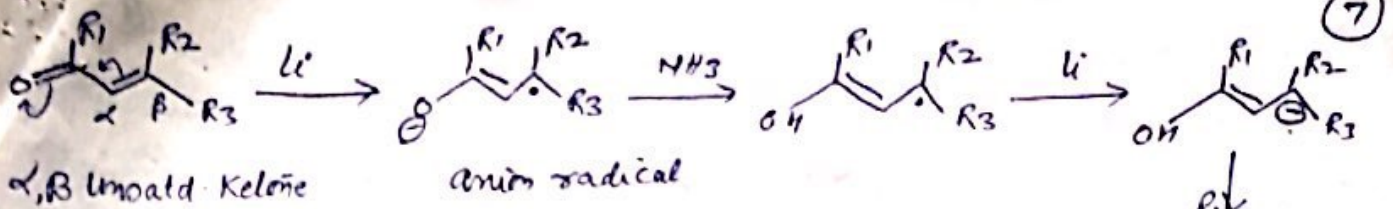


Reduction of α,β Unsatur. Ketone

The reduction under dissolving metal conditions, leads to the enolate of corresponding saturated ketone. Mech. involves following steps -

- ① Formation of anion radical after uptake of an electron
- ② Anion radical abstracts a proton from ammonia or added alcohol
- ③ The addition of another electron leads to the enolate anion
- ④ When a stronger acid is not present, this anion retains its -ve charge and resists addition of another electron and thus no further red<sup>n</sup> can occur.

Acidification with NH<sub>4</sub>Cl, gives the saturated ketone.

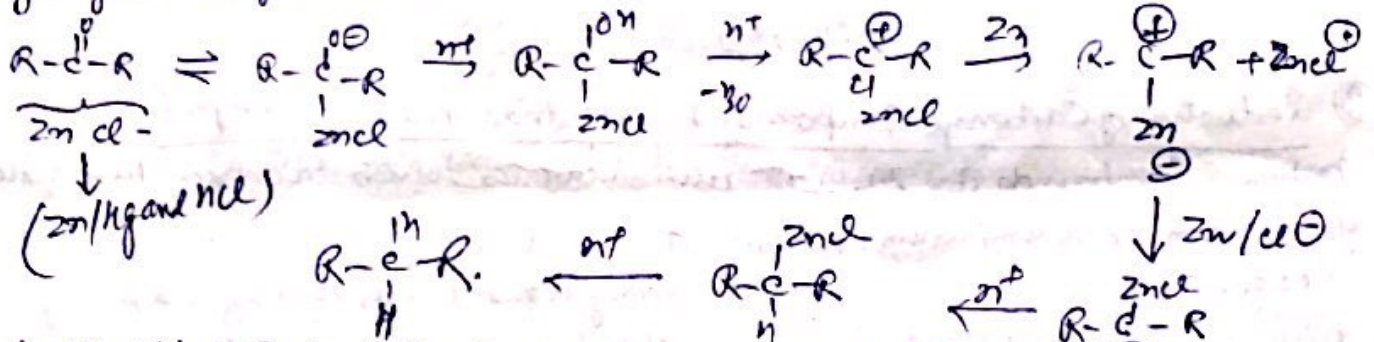
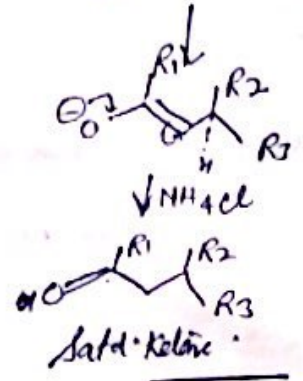


Reductive deoxygenation of Carbonyl groups

Various Carbonyl Compounds are reduced to methylene Compounds by a no. of methods. Some of them are -

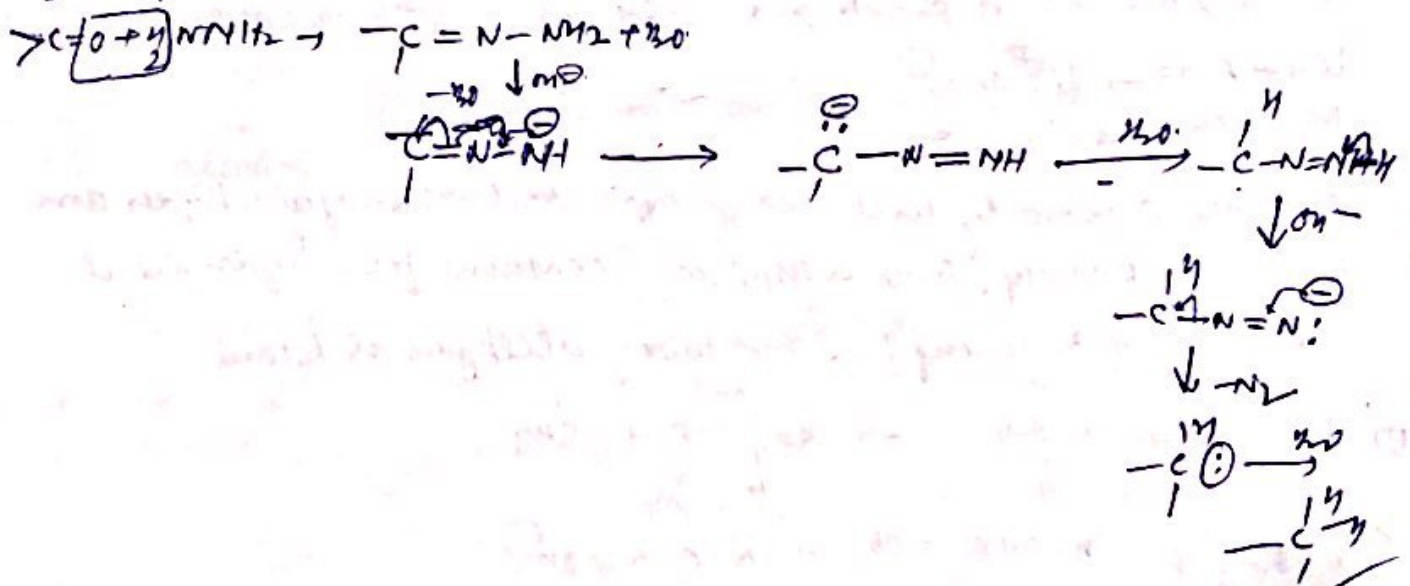
① Clemmensen's method

Zn-Hg/HCl, Amalgamated zinc and HCl is a classical reagent for conversion of carbonyl group to methylene group. mechan may involve carbon-zinc bond at the metal surface. Transfer of electrons from metal surface to carbonyl carbon atom has been suggested. Conc. acid helps about initial protonation. Amalgamated zinc has its hydrogen overvoltage so that molecular hydrogen not generated.



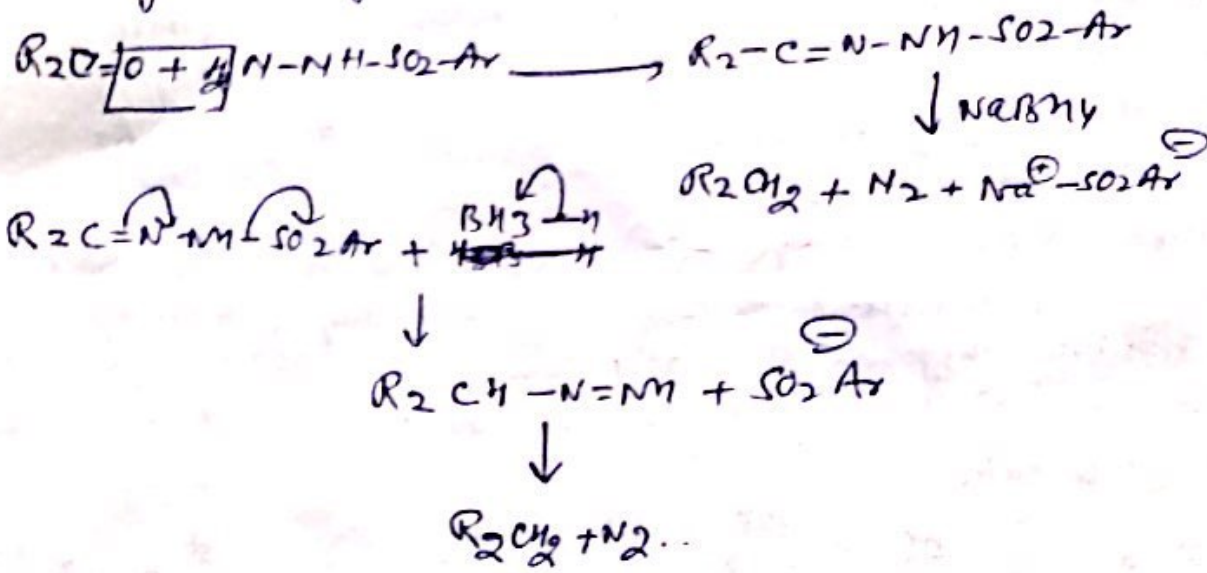
② Wolff-Kishner Reduction

In this method the substrate is heated with hydrogen hydroxide and a base (NaOH or KOH) - The Huang-Minlon modification in which the reaction is carried out in refluxing diethylene glycol has completely replaced the original procedure.



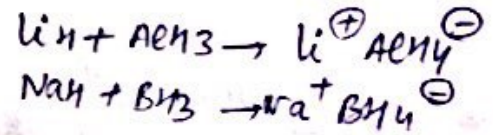
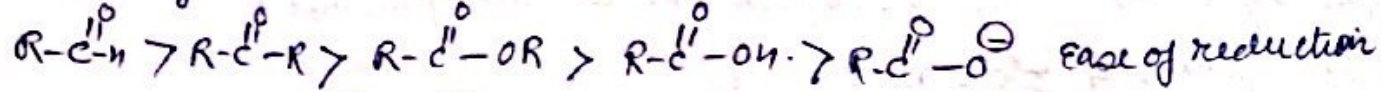
3) Toluid-hydrazone method

A Carbonyl Compound reacts with Toluidene-p-sulphonyl hydrazine to give corresponding Toluid-hydrazone. which on reduction with NaBH4 converts the carbonyl group to methylene group. The mech. involves formation of diimide as in Wolf-Kishner method.

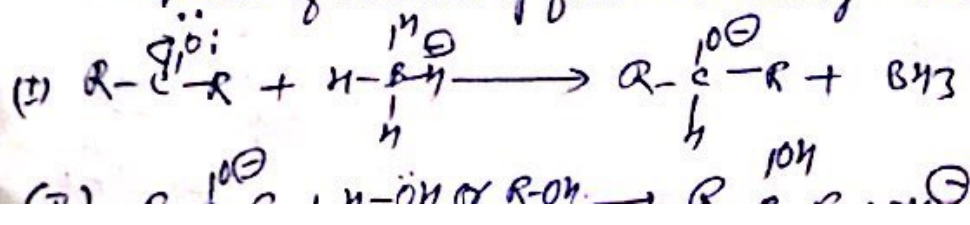


4) Reduction of Carbonyl Compounds by Hydride Transfer reagents

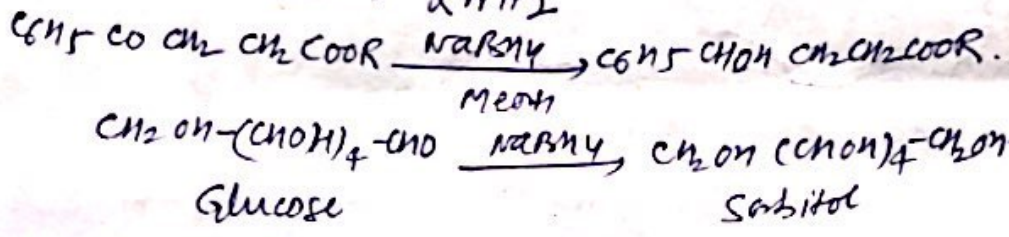
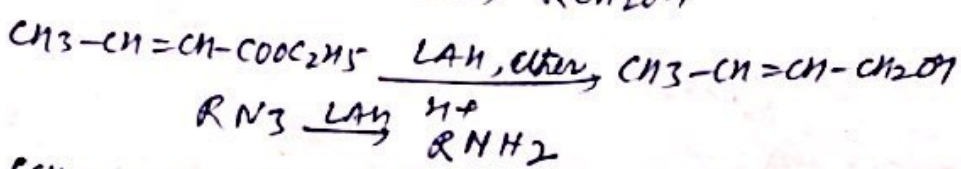
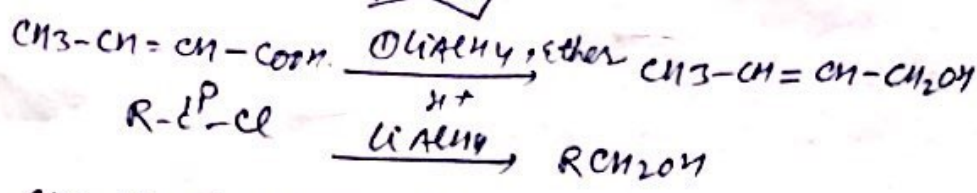
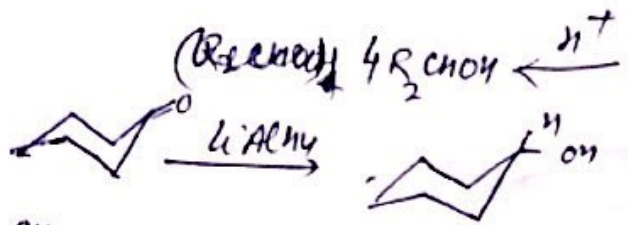
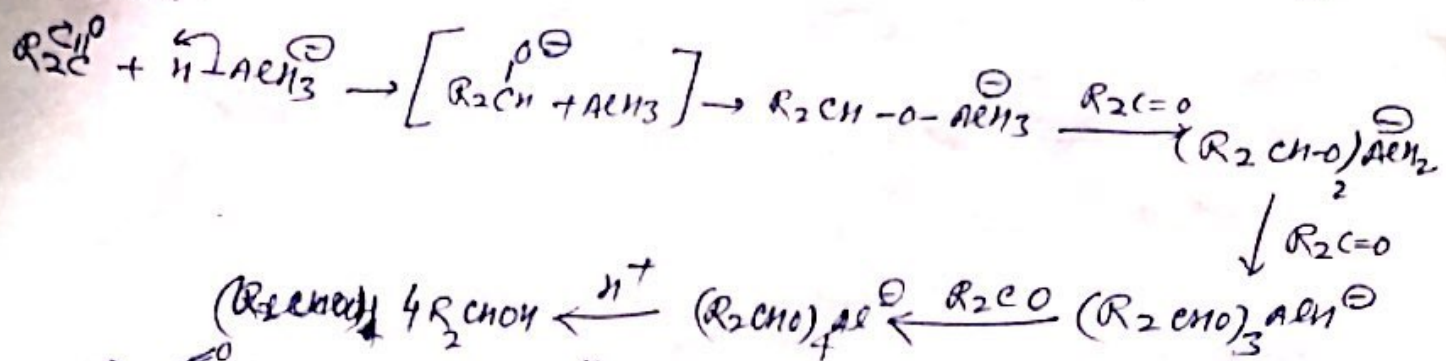
Carbonyl Compounds are reduced with reagents which transfer hydride from boron or aluminium. NaBH4 and LiAlH4 are most widely used reagents. NaBH4 is a mild reducing agent which reacts rapidly with aldehydes or ketones, but only slowly with esters. LiAlH4 is a more powerful hydride donor reagent, which reduce esters, acids, amides and nitriles along with aldehydes and ketones. But none of these reagents react with carbon-carbon double bonds.



The most commonly used reagent for reduction of aldehydes and ketones is NaBH4. Since a BH4- ion contains four hydrides it is capable of reducing four molecules of aldehydes or ketones



LiAlH<sub>4</sub> reduction are carried out in aprotic solvents, as it reacts violently with water, NaBH<sub>4</sub> reactions can be carried out in water or alcohol solution.



Reduction by dissolving metals:

These reductions take place by ~~direct~~ transfer of electrons from the metal and a proton donor which may be water, alcohol or an acid. 1st group metals such as Li or Na give up their outer shell electron easily and dissolve in solvents such as NH<sub>3</sub> (liq.) or alcohol.

Sodium-alcohol:

The easiest method of reducing ketones is with Sodium-alcohol.

