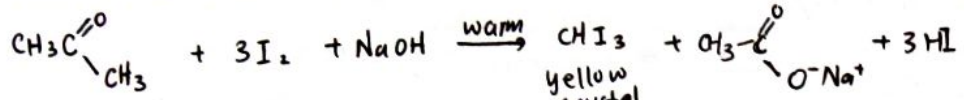
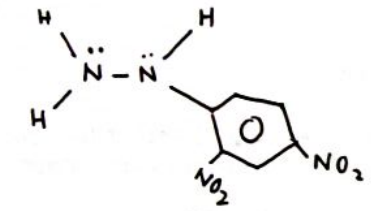
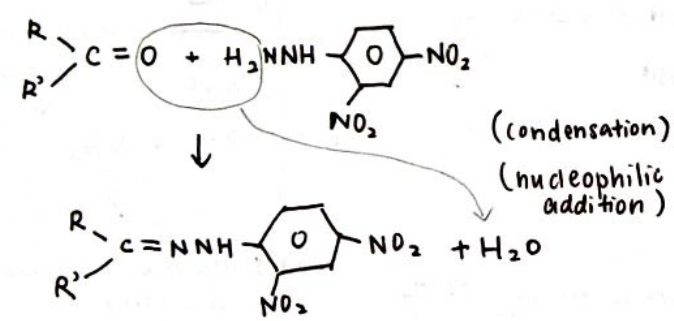
Aldehydes AND ketones (CARBONYL COMPOUNDS)

TRI-IODOMETHANE REACTION (IODOFORM)

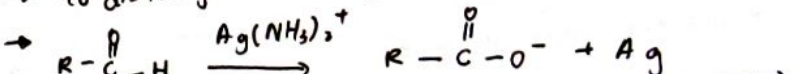
- test for CH_3CO- group
- same as 2° alcohol, just starting from 2nd step
- 
- reagent: $I_2(aq)$, $NaOH(aq)$
- conditions: warm

2,4-DINITROPHENYLHYDRAZINE

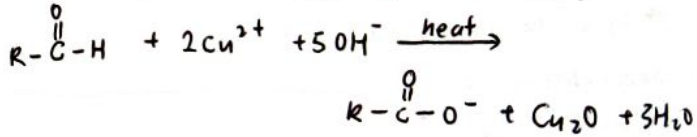
- reacts w/ carbonyl compounds to form 2,4-dinitrophenylhydrazones.
- 
- 

- reagent: 2,4-dinitrophenylhydrazine
- conditions: room temp
- forms orange ppt
- products have sharp characteristic melting pts.

TOLLEN'S REAGENT ($Ag(NH_3)_2^+$)

- oxidises aldehydes to **c. acids**
- itself reduced to silver mirror.
- to distinguish aldehydes from ketones
- 
- conditions: 60°C water bath
  OR

FEHLING'S SOLUTION (copper II tartrate) blue solution

- oxidises aldehydes to **c. acid**
- itself reduced to Cu_2O ($Cu^{2+} \rightarrow Cu^+$)
- 
- conditions: warmed in water bath

LITHIUM TETRAHYDRIDOALUMINATE / SODIUM ($LiAlH_4$) / ($NaBH_4$)

(continued)

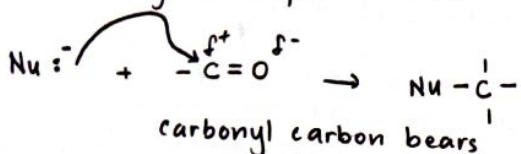
- reduces aldehydes to 1° alcohols
- reduces ketones to 2° alcohols
- opposite of oxidation w/ $K_2Cr_2O_7$
- reagent: $LiAlH_4$
- conditions: in dry ether, heat
- $LiAlH_4$ reacts violently w/ H_2O → so needs to be dry
- $NaBH_4$ used because, less powerful ∴ $ ↓, & can be used in H_2O or alcohol solutions.

* can also use hydrogen (same as hydrogenation) but non specific.

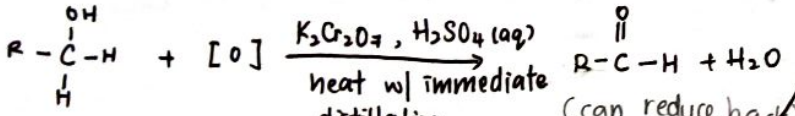
* $LiAlH_4$ specific for:
- aldehydes → 1° alcohol
- ketones → 2° alcohol
- CN (nitriles) → CH_2NH_2
- c. acids → 1° alcohol (But not for ester + c. acid)

$NaBH_4$ ← too weak

Aldehydes AND Ketones (CARBONYL COMPOUNDS)

- have many reactions in common
- both undergo nucleophilic addition
- 
  carbonyl carbon bears a partial +ve charge.
  * not the same as C=C because there is dipole.
- aldehydes more reactive than ketones
  - ↳ carbonyl C more +ve
  - ↳ " less sterically hindered
- C bond to more alkyl group = less reactive (stable cuz less +ve)
- in aldehydes, carbonyl must be C_1.
- sp^2
- bp ↑ due to pd-pd

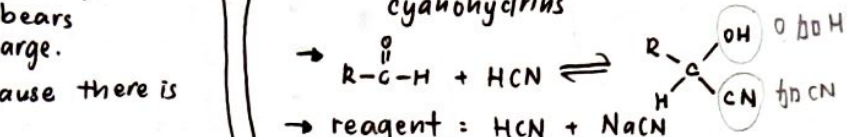
PREPARATION OF ALDEHYDES

- oxidation of 1° alcohols
  
  (can reduce back)
- reagent : $K_2Cr_2O_7$ in dilute H_2SO_4
- conditions : heat w/ continuous distillation

PREPARATION OF KETONES

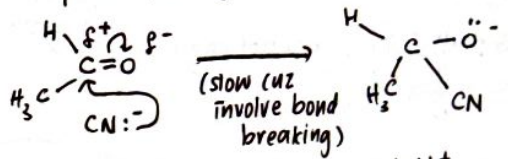
- oxidation of 2° alcohols (can reduce back)
- reagents : $K_2Cr_2O_7$ (aq), H_2SO_4 (aq) or $KMnO_4$ (aq), H_2SO_4 (aq)
- conditions : heat
- oxidation of alkenes (aldehydes cannot because will directly become carboxylic acid).
  - ↳ reagent : $KMnO_4$, H_2SO_4 (aq)
    Conditions: Heat.

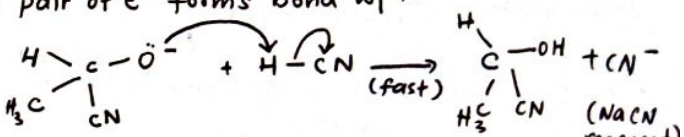
CHEMICAL PROPERTIES

- add hydrogen cyanide (HCN) to carbonyl group to form - 2 - hydroxyalkanenitriles / cyanohydrins
- 
- reagent : HCN + NaCN (catalyst)
- useful intermediates.
  → nucleophilic addition

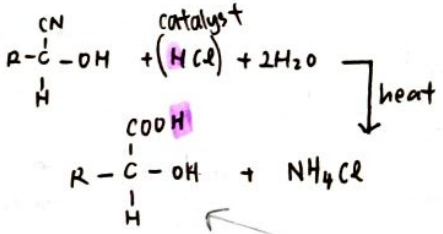
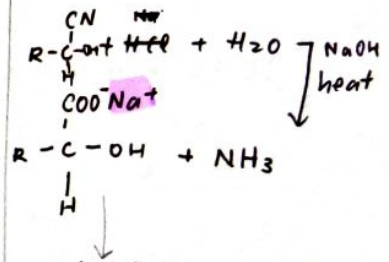
PRODUCTS OF NUCLEOPHILIC ADDITION

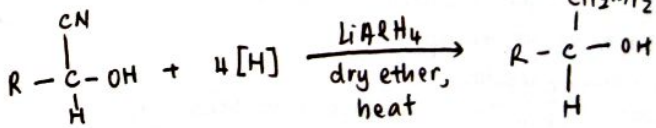
- since planar, CN^- attack above or below equally
- ∴ equimolar mixture
- all aldehydes

- mechanism :
- ① → generation of nucleophile CN^-
  $NaCN \rightarrow Na^+ CN^-$
- ② → CN^- attacks slight +ve carbon, one bond in C=O breaks.
  - → a pair of e^- goes to O
  

- ③ → pair of e^- forms bond w/ H^+
  

reaction of products (hydrolysis)

- can be hydrolysed by :
- → dilute HCl to a C. acid
  
- → NaOH (aq) + H_2O to carboxylate salt
  
  add dilute HCl to remove Na^+ and form

- can be reduced by $LiAlH_4$
- 
- → H_2 + Ni + heat also can, but non specific & weak
- → $LiAlH_4$ strong and specific for 2-hydroxy alkane nitriles and carbonyl compounds.