UNIT-IV – Organic Functional Group Analysis

classificatn of organic

Organic functional groups are classified into 3 catagories such as

1. Acidic functional Groups — Thiols, enols, & phenolic hydroxyl
2. Basic functional Groups – Aliphatic & Aromatic 1°, 2°, & 3°- amines, hydrazine derivatives
3. Neutral functional Groups — Aldehydes, ketones, olifinic, Nitro & methoxy

1. Acidic Functional Groups :-

a) Phenolic Hydroxyl Group :-

Phenolic Hydroxyl Group is determined by two methods such as 1. Brominatn Method 2. Acetylatn Method

1. Bromination Method :-
   1. Reagents
   2. Preparatn
   3. Principle
   4. Procedure.
   5. Calculatn (or) Report.

1. Reagents :-
   1. 0.2 N Potasium bromate - bromide soln ($KBrO_3$-K B
   2. Phenolic Hydroxyl Group (sample)
   3. Conc. HCl
   4. 10 % NaOH
   5. 20 % KI

6. 0.1 N sodium thiosulphate . ($+1\frac{1}{4}PO$) ($Na_2S_2O_3$)

7. starch indicator sol^n

2. Preparat^n of Reagents :

Preparat^n of 0.2 N. Pottasium Bromate - Bromide sol^n

Dissolve 5.567 gms of AR. pottasium Bromate & 75 gms of pure pottasium bromide in water dilute to 1 lit in a volumetric flask. The large excess over five equivalence of pottasium Bromide serves to insure the complete Reduct^n of the bromate when the sol^n is acidified & also to increase the solvent power of the sol^n for free bromine liberat^n

Preparat^n of 0.1 N sodium thio solphate

Dissolve about 25 gms of AR. sodium thio sulphate Penta hydrate in 1 lit of freshly boiled & cooled distiled water.

Standardise the sol^n with AR. Pottasium dichromate or Pottasium hydrogen pthalate or KI

Preparat^n of STARCH

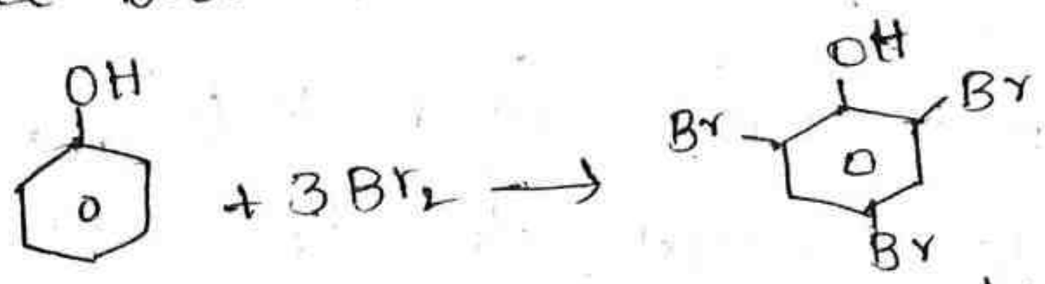
Make a paste of 1 gm of soluble starch with a little water & pour the suspenssion with constant stirring into 100 ml of boiling water.

3. Principle :-

Brominat^n with excess of a standard bromate bromide sol^n in the presence of HCl

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O.$$

The phenolic hydroxyl group reacts with ~~free~~ three bromine molecules yields 2,4,6 tribromo phenol



2,4,6 tribromo phenol

The excess of bromine is determined by the addition of KI soln & titration of the liberated iodine with with standard sodium thio sulphate soln by using starch as Indicator

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

Pott. Iodide — Iodine

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Sodium thio sulphate — Sodium thio sulphide

Conclusion :-
the best results are obtained at Room temp

Procedure :-

1. wt. out accurately about 0.25 gms of a phenol, dissolve it in 5 ml of 10% NaOH soln & dilute the soln to 250 ml in a V.F
2. Pipette out 25 ml of the phenol soln into a 500 ml Iodine flask, followed by 25 ml of the pot bromate bromide soln, & then dilute with 25 ml of water
3. Add 5 ml of conc. HCl, & stopper the flask immediatly shake the flask for 1 min to mix the reactants, & allow to stand for 30 mins with occational stirring of the contents of the flask.
4. cool the flask under tap or ice water, place 10 ml of 20% KI soln & stopper the flask, shake

the flask well for 30 sec & allow to stand for 10 mins

5. Remove the stopper & wash the neck of the flask with a little water, titrate the free iodine which is equal equivalent to the excess of bromine taken, with 0.1 N hypo soln, add about 1 ml of starch soln near the end point

Blank:- carry out a blank analysis using 25 ml of the bromate-bromide reagent, 25 ml of water & the procedure being identical with the analysis Proper

Calculatn:

$$\% \text{ of purity of phenol} = \frac{(V_1 - V_2) N_1 \times m \times 100}{w \times 2000 \times z}$$

where V_1 = Vol. of the hypo soln is used for blank

V_2 = Vol. of the hypo soln is used for sample

N_1 = Nor. of hypo soln

m = Mol. wt of the sample / phenol

w = weight of the sample / phenol

z = No. of Br atoms substituted in the phenol

Acetylation Method :-

Reagents :-

1. Phenolic hydroxyl Group
2. Acetic anhydride in pyridine
3. alc. NaOH
4. Mixed indicator
5. 10% NaOH

Preparatn of Reagents

Preparatn of Acetic Anhydride in Pyridine :-

Mix one volume of acetic anhydride (AR) & three volumes of pure, dry pyridine as required

Preparatn of alk NaOH (0.5N) :-

Mix the required volume of saturated aqueous NaOH soln with ethanol or Methanol in a 500ml V.F the methanolic soln is generally

Preferred because of its better keeping properties,

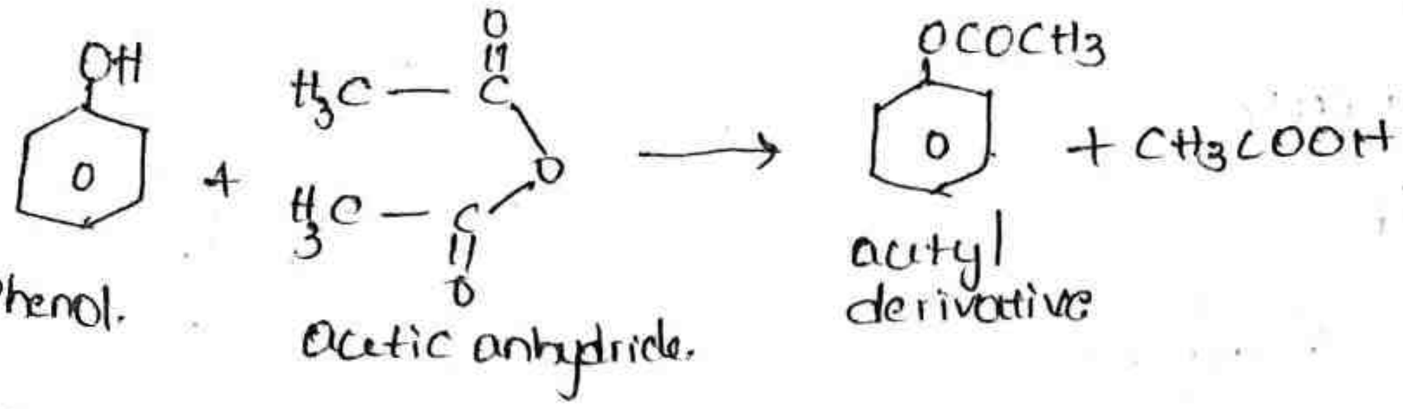
standardise the alcoholic alkali with AR potassium hydrogen Pthalate or with standard 0.5 N aq. H_2SO_4 using the mixed indicator

Preparatn of mixed Indicator soln

Mix one part of 0.1% aq cresol red neutralised with NaOH soln & 3 parts of 0.1% aq. Thymol Blue neutralised with NaOH

The colour change is at a pH of about 9.8

Principle :- The acetylatn method involves the replacement of the hydrogen on an phenolic hydroxyl group by acetyl group. The reagent consists of a soln of acetic anhydride in pure pyridine & is used in excess



Phenol. Acetic anhydride. acetyl derivative

The addition of water converts the excess of acetic anhydride into acetic acid, the total free acetic acid is then titrated with NaOH soln

$$(CH_3CO)_2O + H_2O \longrightarrow 2CH_3COOH$$

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O.$$

The imp step in acetylatn is that pyridine is used as a solvent in acetylations because it is inactive towards the reagents, it removes the acid products by salt formatn, & it also serves as a catalyst

$$Ar\text{-}OH + (CH_3CO)_2O + C_5H_5N \rightarrow ArOCOCH_3 + CH_3COO^- \cdot C_5H_5NH^+$$

Procedure :-

1. Accurately weighed sample contain 1 to 2.5 milli equivalents of the sample into a 250 ml Iodine flask & add 3 ml of the acetylating reagent
2. Stopper the flask, heat the flask on a steam bath for 45 mins
3. Add 5-6 ml of water & shake the flask for uniform

mixing & heat for 2 mins more.

4. cool the flask under running water or in ice. & add few drops of mixed indicator & titrate the contents with 0.5N alc. NaOH to a grey colour

Blank :- Make a blank determinatn on 3 ml of the reagent simultaneously & similar in all respects except for the addition of sample. The diff b/w the volumes of alkali used in the two titrations corresponds to the alcohol which has reacted

Calculatn :

$$\% \text{ of hydroxyl Group} = \frac{(V_1 - V_2) \times N_1 \times m \times 100}{w \times 1000}$$

where, V_1 = Vol. of NaOH soln used in blank.

V_2 = Vol. of NaOH soln used for sample.

N_1 = Nor. of alk NaOH

M = mol. wt of the sample.

w = wt. of the sample.

(b) Thiols (Mercapto Group / Mercaptain)

Thiols are determined by 2-methods

1. Iodine method (Oxidatn method)
2. Ppecipitatn / Argentometric method.

1. Iodine Method

Reagents:

- Sample (R-SH)
- Iodine soln (0.1 N)
- Hypo (0.1 N)
- Starch
- Benzene.

Preparatn of reagents

1. Preparatn of 0.1N Iodine soln

Dissolve 20 gms of Iodine free Potassium iodide-free (AR) in 40 ml of water in a glass stoppered 1 lit volumetric flask

(or)

weighing out about 12.7 gms of AR Iodine on a watch-glass on a rough balance & transfer it by means of a small dry funnel into the 1000 ml V.F & make up with distiled water.

The resulting soln is best stored in a dark glass stoppered water, it may be standardised with (AR) Arsenious oxide (or) with standard 0.1 N Sodium thio sulphate soln

2. 0.1 N hypo soln
3. Preparatn of starch indicator

Principle :

A principle involved in the iodine method is iodine oxidises thiols to disulphides

$$2R\text{-}SH + I_2 \longrightarrow R\text{-}S\text{-}S\text{-}R + 2HI$$

Thiol → disulphide

A soln of the mercaptain is treated with a measured excess of standard iodine soln & after reactn is complete the excess of iodine is titrated with standard hypo. soln by using starch as Indicator

$$I_2 + 2NaS_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Sodium Iodide. Sodium tetra thionate

Procedure :

1. weigh out accurately about 0.2 gms of the mercaptan in a sealed glass ampoule (e.g:- n-octyle mercaptan, n-decyle mercaptan or n-dodecyl mercaptan)
2. & place it in a 500 ml iodine flask together with a few glass beads to aid in a breaking the ampoule
3. pippete out 50 ml of the standard 0.1 N iodine soln into the flask, stopper the flask & shake it vigorously for 5 mins more, introduce 20 ml of absolute ethanol & shake for a further 10-15 mins
4. Titrate the excess of iodine with standard 0.1 N sodium thiosulphate soln using starch indicator near the end point.

Blank :

carry out a blank determinatn with 50 ml of the iodine soln

calculatn :

$$\% \text{ of purity of Mercapto Group} = \frac{(V_1 - V_2) \times N_1 \times M \times 1000}{\omega \times 1000}$$

V_1 = vol. of hypo used for blank

V_2 = vol. of hypo used for sample

N_1 = Nor. of hypo.

M = mol. wt of sample

ω = wt. of sample

2. Precipitatn Method

Reagents

1. Sample (RSH)
2. Silver Nitrate (0.005 N)
3. Ammonium thio cyanate (0.005 N)
4. Ferric Alum
5. Benzene.

Preparatn of Reagents

1. Preparatn of ferric Alum : soln :

Dissolve 4 gms of AR ferric Alum in 10 ml of conc. Nitric acid, boil the soln to remove oxides of Nitrogen, cool & dilute with 30 ml of distilled water.

Principle :-

The procedure is based upon the precipitatn of a soln of the thiol with a measured excess of standard silver nitrate soln, followed by titratn of the excess of reagent with standard Ammonium thiocynate soln using a ferric alum as indicator.

$$R\text{-}SH + AgNO_3 \rightarrow R\text{-}SAg + HNO_3$$

Procedure :

weigh out accurately 1-2 milli equivalence of the mercaptan & dissolve it in 100 ml of pure benzene in a V.F.

* Pippete out 10 ml of sample soln into a 250 ml conical flask containing 10 ml of anhydrous ethanol
* Add about 45 ml of the 0.005 N silver nitrate soln from a burette to the sample soln, stir the soln by using magnetic stirrer.
* Then add 2 ml of the ferric Alum indicator & titrate the soln with 0.005 N Ammonium thiocynate until a faint pink colour is observed
* Discharge the pink colour by adding a excess of the standard silver nitrate soln, restore the pink end point. by adding the standard Ammonicum thiocynade soln drop wise.
* It is imp that soln be continously stirred during the titratn

some experience is required in determining the exact end point, the pink colour is more clearly observed

Blank:

Run a blank determinatn on the readings

Calculation:

$$\% \text{ of } R\text{-}SH = \frac{V_1 \times N_1 \times 33.07 \times 100}{w \times 1000}$$

where

V_1 = Net vol. of $AgNO_3$ soln used for the sample

N_1 = Nor. of the $AgNO_3$.

w = wt. of the sample.

c) Enols

1. Bromnatn method:-

Reagents

1. Sample
2. Methanolic Bromine soln
3. 10 % KI / HI
4. Hypo (0.1 N)
5. Starch indicator.
6. Di iso butylene.

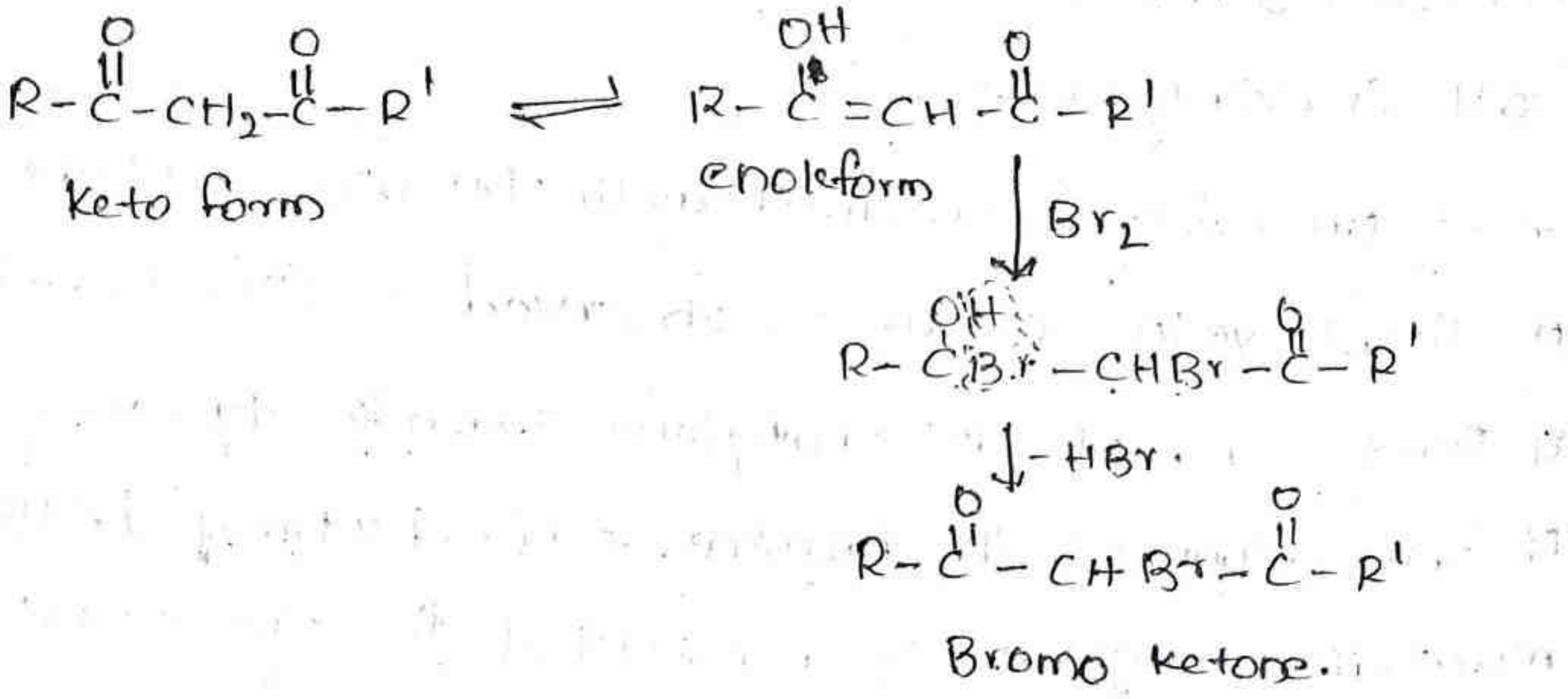
Preparatn of 0.1 N methanolic Bromine soln

Disolve 2 gms of dry (AR) Bromine in 250 ml of anhydrous methanol. the soln must always be Prepared immediatly before used

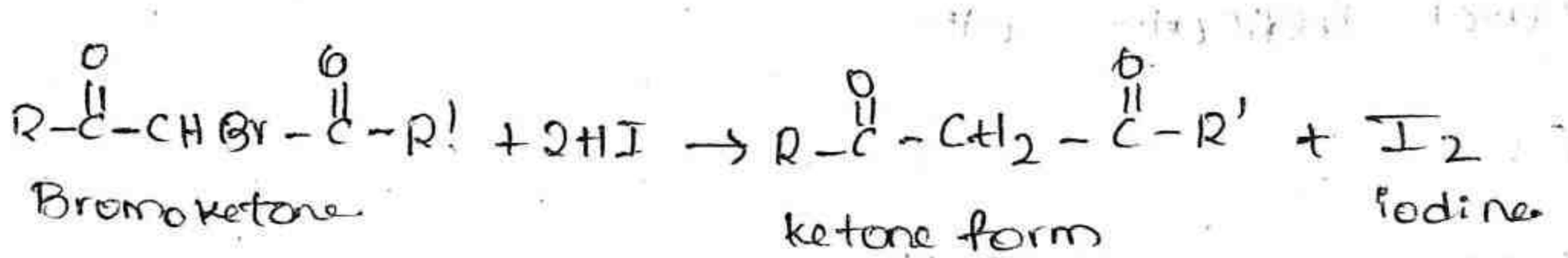
Principle

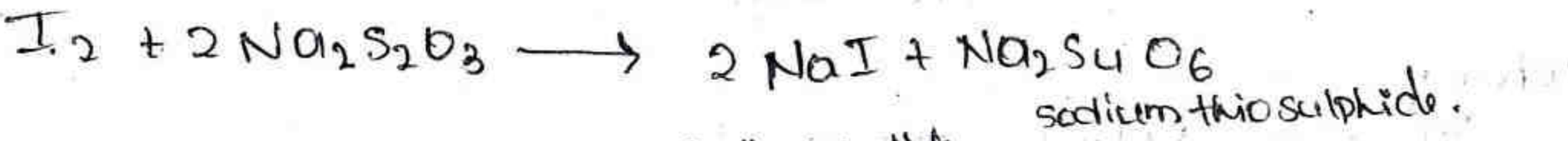
The enol form generally reacts with bromine much more rapidly than keto form. By adding an

excess of alcoholic soln of bromine rapidly to a tautomeric mixture. In the same solvent. solid, removing the excess of bromine with diisobutylene a bromo ketone is formed



The Bromoketone may be Reduced quantitatively with hydroiodic acid (HI) & the liberated iodine determined by titratn with a standard soln of sodium thio sulphate.





The accuracy of the method depends largly upon the speed with the excess of bromine is removed

Procedure:

1. weigh out accurately 1.2 - 1.6 gms of the sample (e.x- ethyl acetoacetate, acetylacetone or dibenzoylmethane)

dissolved it in ~~abs~~ absolute methanol & dilute to 100ml with absolute methanol in V.F.

2. Transfer 25 ml of sample soln to a dry 150ml conical flask, & cool to -5°c to -10°c in an ice salt freezing mixture

3. Add an excess of the methanolic bromine soln until a faint yellow colour is observed & stirr the mixture & pour 3 ml of diisobutylene. immediately, mix well if the colour of the bromine is not discharged, add more diisobutylene., it is essiential for the sucess of the brominatn method.

4. Now, add 5 ml of the ~~Pe~~ HI/KI soln, warm to 30°c on a water bath, allow to stand for 5 mins, & titrate the liberated iodine with standard 0.1N hypo using starch indicator soln

Calculation :-

$$\% \text{ of enole} = \frac{V_1 \times N_1 \times M \times 1000}{2 \times w \times 1000}$$

where,

V_1 = ~~wt~~ vol. of hypo soln

N_1 = Nor. of hypo soln

M = mol. wt of sample

w = wt. of the sample

2. Basic functional Group

Amines :- (Aliphatic & Aromatic 1° & 2°-Amines)

a) Determinatn of amines ~~by~~ (1°-aromatic amine or auiline) by brominatn

Reagents :-

1. sample (1° aromatic auiline)
1. Potassium bromate - Bromide soln
2. 20% KI
3. conc. HCl
4. Hypo ($Na_2S_2O_3$)
5. starch indicator

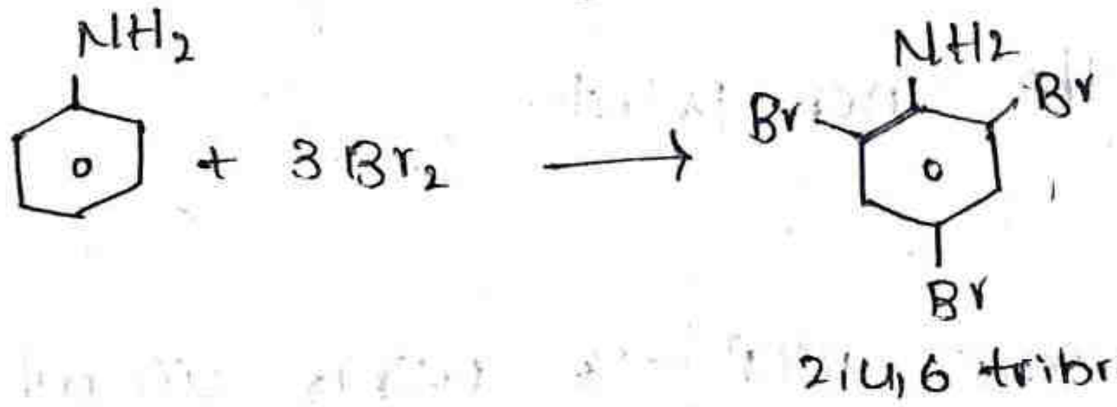
Preparation of Reagents

Preparatn of above reagent as well as brominatn of Phenolic hydroxyl Group

Principle :-

Brominatn with excess of a standard bromate-bromide soln in the presence of hydrochloric acid, aniline yields 2,4,6 tribromo aniline.

$$KBrO_3 + 5KBr + 6HCl \longrightarrow 3Br_2 + 6KCl + 3H_2O$$



2,4,6 tribromo auiline

The excess of bromine is determined by the addith of KI soln & titratn of the liberated Iodine with standard thiosulphate soln using starch as indicator

$$Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

$$I_2 + 2NaS_2O_3 \xrightarrow{\text{Starch}} 2NaI + Na_2S_4O_6$$

Procedure :-

* Weigh out accurately about 0.25 gms of the amine (aniline) into a 250 ml V.F dissolve the sample in the minimum volume of HCl, & dilute to the mark with distilled water.
* Pippete out 25 ml of the amine soln into a 500 ml iodine flask, followed by 25 ml of the bromate bromide soln, dilute with 25 ml of, add 5 ml of conc. HCl & stopper the flask immediatly. Shake the flask for 1 min to mix the reactants, & allow to stand for 10 mins.
* Cool the flask under tap or an ice-water, & place 10 ml of 20% KI soln, shake the flask for 30 secs & allow to stand for 5-10 mins
* Remove the stopper, titrate the free iodine with standard 0.1N hypo, using 2 ml of starch indicator near the end point.

Blank:

Carry out a blank analysis using 25 ml of the bromate-Bromide soln & 25 ml of water.

Calculatn

$$\% \text{ of purity of aniline} = \frac{(V_1 - V_2) \cdot N_1 \times M \times 100}{w \times 1000 \times Z}$$

V_1 = vol. of hypo required for blank

V_2 = vol. of hypo required for sample

N_1 = Nor. of hypo

M = mol. wt of sample

w = wt. of sample

Z = No. of bromine atoms substituted on aniline ring

9) Determinatn of 1° & 2° aliphatic amines by (Acetylation) Acetic Anhydride in pyridine method.

Reagents:

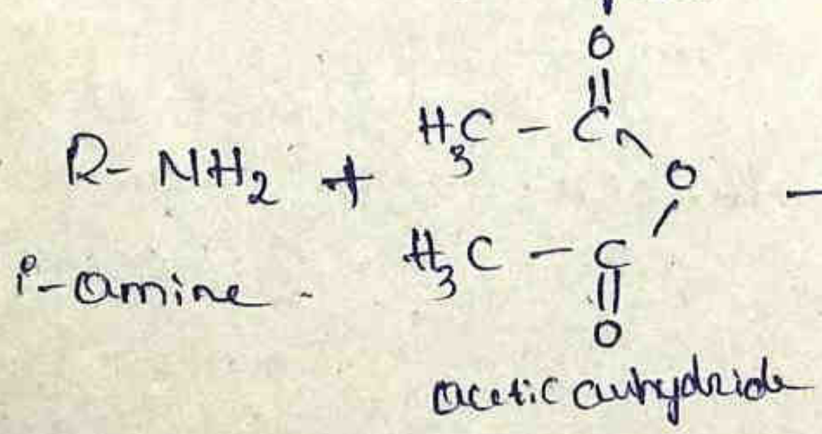
1. Sample (1° & 2° Aliphatic amines)
2. Acetic Anhydride in pyridine.
3. alcoholic NaOH (methanolic NaOH)
4. Mixed indicator
5. dil. HCl.

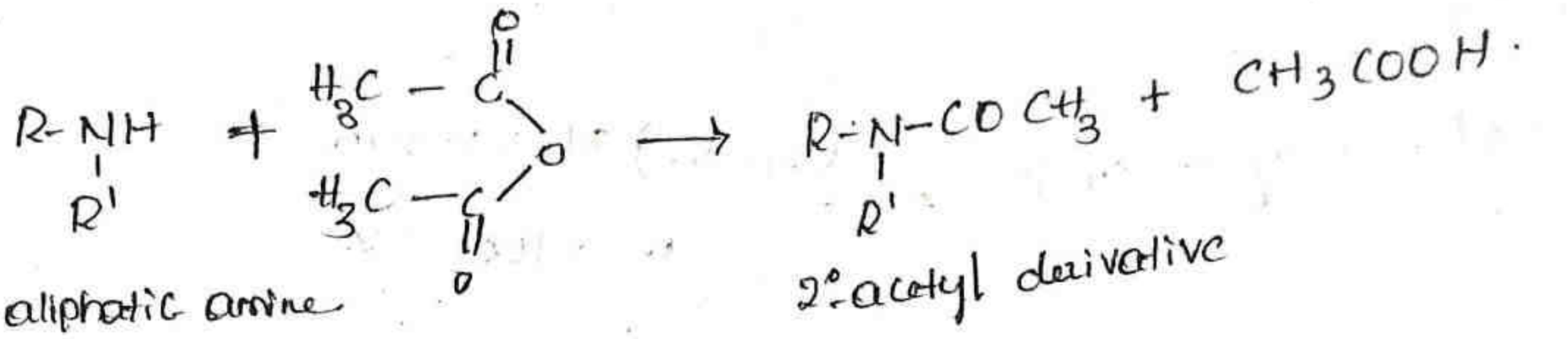
Preparatn of Reagents

As well as acetylatn of Phenolic hydroxyl Group

~~Procedure~~ Principle :-

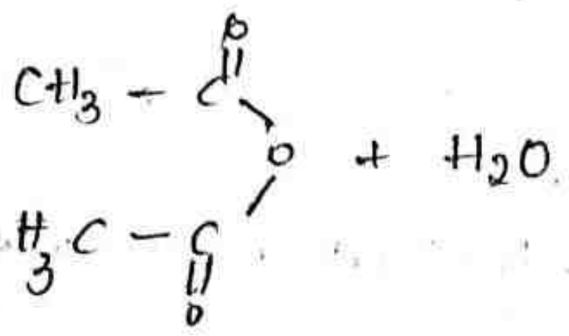
Acetylatn at room temp with an excess of a solⁿ of acetic anhydride in pyridine, the 1° & 2° aliphatic amines on acetylatn gs corresponding acetyl derivative





2° aliphatic amine — 2° acetyl derivative

* the residual excess of acetic anhydride is decomposed by the addition of water

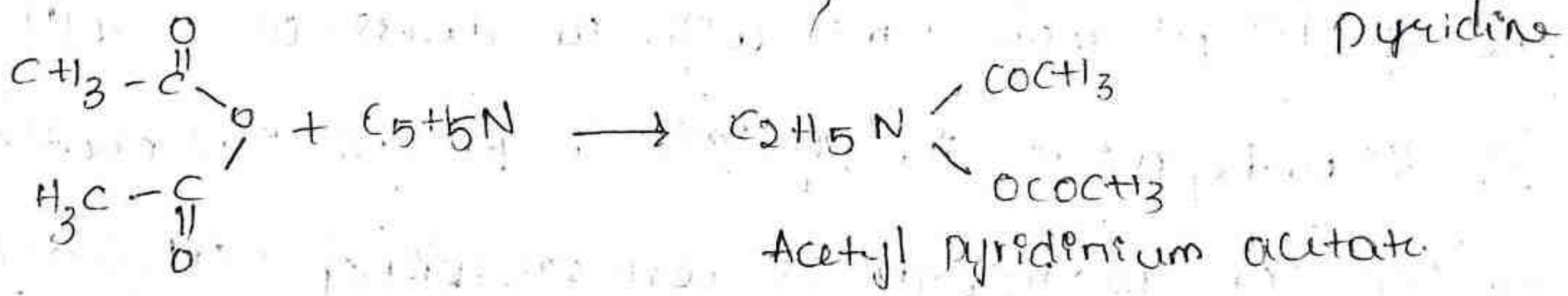


* The total free acid is determined with standard alcoholic NaOH soln by using mixed indicator

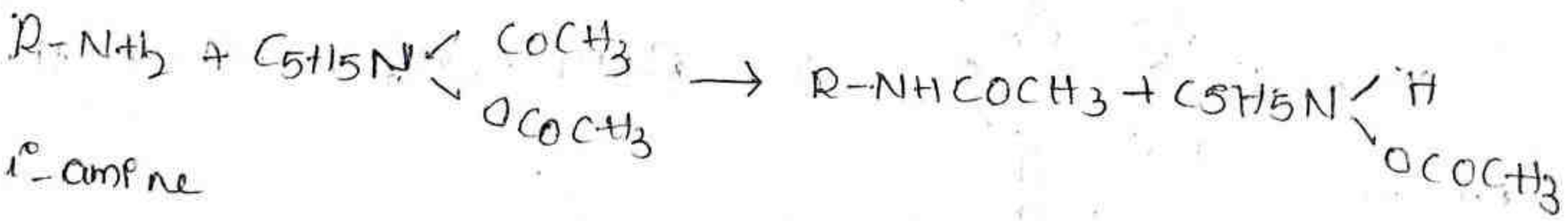
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O.$$

Importance of Pyridine

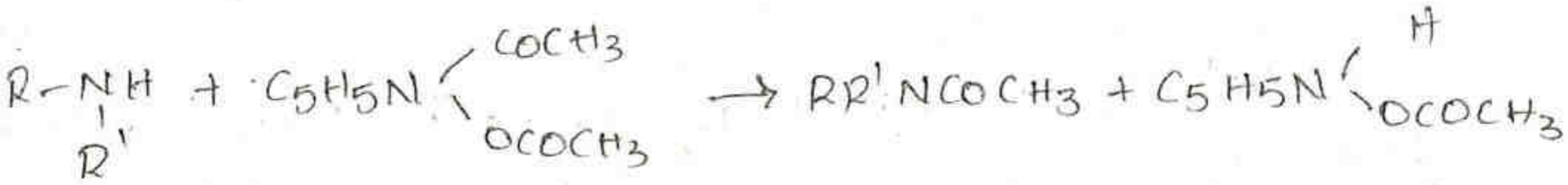
* Acetylation is Quantitative at room temp of about 20% acess of acetic anhydride is used and the reaction mixture is allowed to stand for 30 mins
* Statisfactary results have been obtained with ethylamine, isopropyl amine, n-butyl amine, n-heral amine, ethyldiamine, Diethyl amine, Di n-butal amine, aniline, n-napthal amine & n-methyl amine in the presence of Pyridine



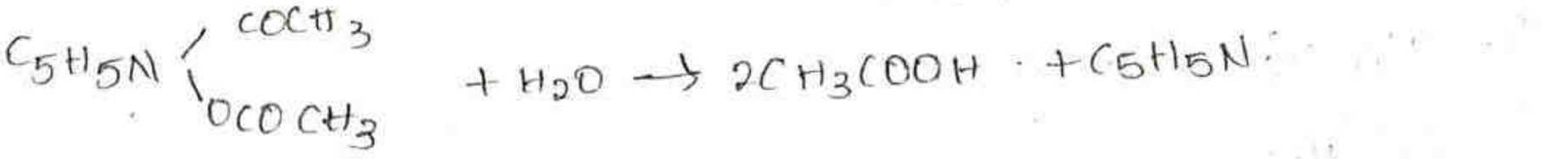
Acetyl pyridinium acetate



1° amine



2^{o} -



Procedure :-

* Introduce a weighed quantity containing about 2 milli equivalence of (sample) i.e. 2° Amine into a 250 ml Iodine flask & add 6 ml of the acetic anhydride in pyridine reagent
* Insert the stopper & allow to stand at room temp with frequent gentle agitatn, cool the flask under tap water, & remove the stopper. add a few drops of the mixed indicator & titrate immediatly with a standard alcoholic NaOH soln to apperance of a blue colour
* The acetyl derivative may remain in soln when water is added.

Blank

Perform a blank determinatn by using 6 ml of the acetylating reagent simutaniously with the experiment on the sample

Calculatn

$$\% \text{ of purity of Amine} = \frac{(V_1 - V_2) \times N_1 \times 16.03 \times 100}{w \times 1000}$$

where V_1 = vol. of alc. NaOH used for blank

V_2 = Vol. of alc. NaOH used for sample

N_1 = Nor. of alc. NaOH

w = wt. of the sample.

Determinatn of azo Group (Hydrazene) by Reductn Method

Reagents

1. Sample (Hydrazene)
2. Glacial acetic acid
3. dil. H_2SO_4
4. Titanous salts (Titanous sulphate, Titanous cl) 0.1N
5. Ammonium thio cyrate (10% I.)
6. 0.1N ferric Ammonium sulphate soln (Fe III)
7. Stream of CO_2

Preparatn of Reagents

1. Preparatn of Titanous chloride (0.1 N)

From metalic titanium, place 12 gms of titanium metal in a 1 lit beaker or flask, add 800 ml of dil. HCl & warm on a water bath until all the metal disolves (about 6 hrs)

2. Preparatn of Titanous sulphate (0.1N)

From metalic titanium place 12 gms of titanium metal in a 2000 ml beaker or flask, add 1200 ml of dil H_2SO_4 & warm on a water bath until all the metal disolves (about 7 hrs)

Principle :-

Azo compounds are quantitatively reduced by titanous salts

$$RN=NR' + 4Ti^{3+} + 4H^+ \rightarrow R\text{-}NH_2 + R'NH_2 + 4Ti^{4+}$$

azo group — titanous salt — Amines

* the azo linkage is more frequently encountered in dyes & di-intermediates (ex:- Methyl Orange)
* soluble azo dyes may be disolved in H_2O, excess of the titanous soln added, the soln boiled in a stream of CO_2 for 3-5 mins (to create inert atmp), & the excess of titanous salt is titrated with 0.1N ferric Ammonium Sulphate soln using ammonium thio cyanide as indicator

Proudure:-

1. Experience in the titratn of azo groups may be acquired by determining the purity of a sample of Methyl orange.
2. weigh out accurately about 0.25 gms of methyl orange into the titratn flask., add 25 ml of H_2O & 25 ml of Glacial CH_3COOH, shake until disolved.
3. Add 25 ml of dil. H_2SO_4, Pass CO_2 for 5 mins to displace air, Run 50 ml of 0.1N titanous salt soln & boil for 5 mins & cool, add 10 ml of 10% Ammonium thiocyrate soln, & titrate with standard 0.1N Ferric ammonium sulphate soln

Blank :-

Run a blank on 50 ml of the titanous salt soln

Calculatn :-

$$\text{Purity of azo Group} = \frac{(V_1 - V_2)\, N_1 * M \times 100}{w \times 1000 \times 4}$$

V_1 = vol. of ferric soln used for Blank

V_2 = " " Sample

N_1 = Nor. of ferric soln

c) Neutral functional Groups

Determinatn of aldehydes & ketones by Oximatn Method.
(or) by hydroxylamine hydrochloride in pyridin

Reagents :-

1. sample (Carbonyl group)
2. Hydroxyl amine hydrochloride soln ($H_2NOH \cdot HCl$)
3. Pyridine Indicator soln (Pyridine + bromo phenol Group)
4. methanolic NaOH soln
5. Preparatn of Reagents

1. Preparatn of $H_2NOH \cdot HCl$ soln (0.5 N)

Dissolve 35 gms of pure $H_2NOH \cdot HCl$ in 160 ml of distiled water & dilute to 1 lit with 95% ethanol

2. Preparatn of pyridine Indicator soln

Mix 0.25 ml of 4% soln of Bromo phenol Blue in alcohol with 20 ml of pure pyridine & dil. to 1 lit in 95% ethanol

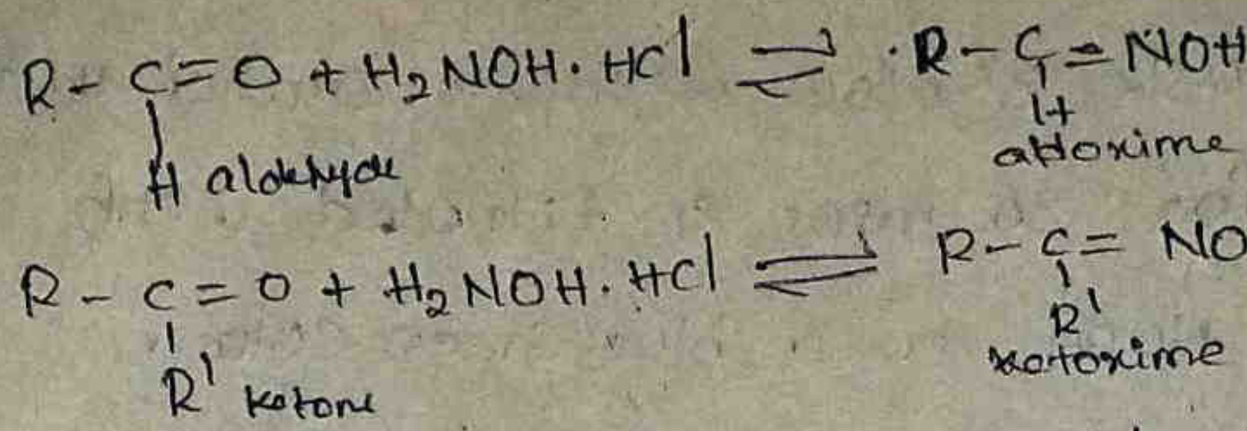
3. Preparatn of Methanolic NaOH soln (0.5 N)

Dissolve 20 gms of AR NaOH Pellates in 100 ml of distiled water & dil. to 1 lit with absolute methanol

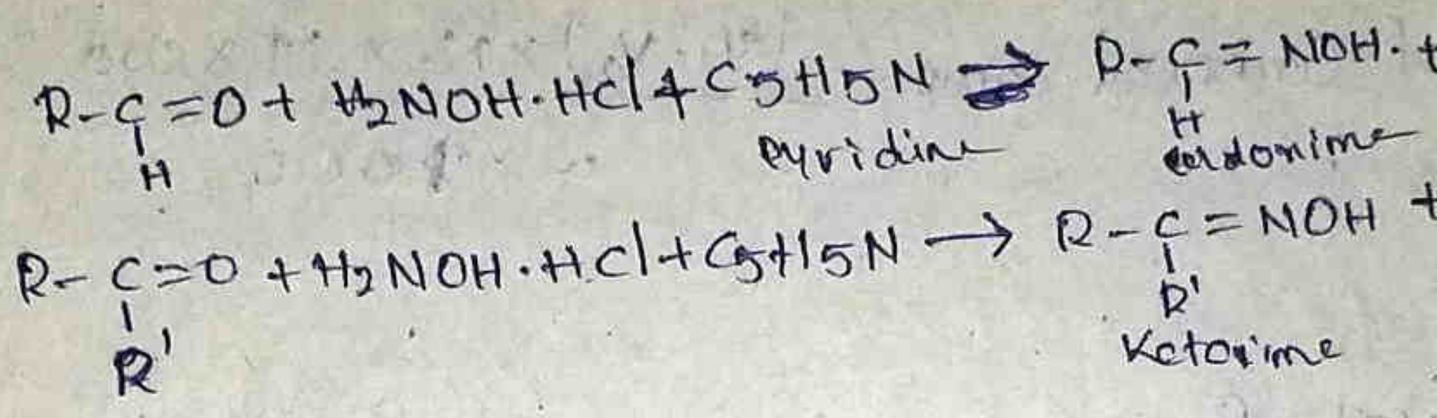
This soln is standardise with standard 0.5 N HCl using bromo phenol Blue as Indicator or with AR Potassium hydrogen phthalate.

PRINCIPLE :-

The most General procedure available for aldehydes & ketones is based on the Oximatn Reactn



The equilibrium of the reversible reactn is displaced to the right in the presence of pyridine & excess of $H_2NOH \cdot HCl$. The pyridine combines with the HCl. to form pyridine hydrochloride.



The pyridine hydrochloride is sufficiently acidic to be titrated with standard NaOH using Bromophenol blue as Indicator

The Rate of Reactn blw a carbonyl compound & hydroxyl amine depending upon the groups R & R'. some compounds ex:- propinaldehyde, furaldehyde, benzaldehyde & acetone. react Quantitatively in 30 mins at the liberated temp in case of acetophenone, benzophenone, benzoin & champhore ~~to~~ may require 2 hrs for complete

Procedure :-

1. Place 30 ml of the $H_2NOH \cdot HCl$ reagent & 100 ml of the Pyridine indicator soln in a 250 ml glass stopper flask & add 10 milli equivalence of aldehyde or ketone accurately weighed

2. stoppers the flask & allow with to stand at the liberated temp for 30 mins & titrated with 0.5 N Methanolic NaOH to a blue-Green colour

Blank

carry out a blank determinatn, omitting the addtn of the carbonyl compound

calculatn:

$$\therefore \%\ \text{purity of carbonyl comp} = \frac{(V_1 - V_2) \times N_1 \times M \times 100}{\omega \times 1000}$$

V_1 = vol. of met. NaOH is required for Blank

V_2 = " " " sample.

N_1 = Nor. of met. NaOH

M = Mol. wt. of sample

ω = wt. of sample.

Determinatn of aldehydes & Ketones by 2,4-DNP (or) Gravametric Method

Reagents:-

1. sample
2. 2,4-DNPH - Di Nitro phenyl Hydrazone.
3. 2N-HCl
4. Preparatn of Reagents

1. preparatn of 2,4-DNPH.

2,4-DNPH is dissolved in 2N-HCl at 0°C

This consists of a saturated soln of pure 2,4-DNPH in 2N aqueous HCl at 0°C, the reagent contains

about 4 mg of the solid per ml

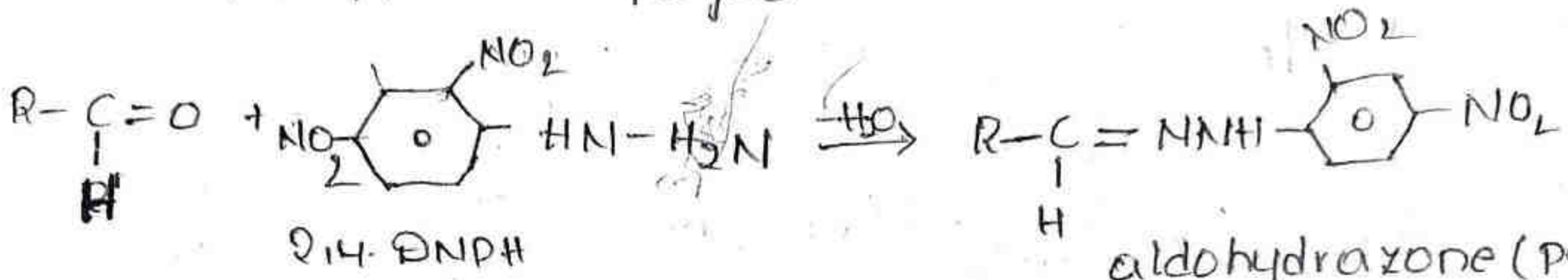
Preparatn of 2N-HCl -

$$N_1V_1 = N_2V_2$$

17.6 ml in 100 ml.

Principle

A standard identificatn reactn for carbonyl compounds with 2,4-DNPH is employed



* A large excess of the Reagent (2,4-DNPH) in aqueous 2N-HCl is used, & the ppt is collected after standing at Room temp for 1 hr
* the derivative can usually dried at 100-110°C, for best Results vaccume discator is Recomended

Procedure:-

1. Place 50-60 ml of the reagent in a 250 ml Glass stoppered conical flask, & add 0.02 to 0.04 milli moles of aquerately weighed of the sample
2. Shake the flask for 2-3 mins to ensure that the carbonyl compounds disolves, allow to stand for

1 hr in an ice bath, shaking occationaly

3. Decant through a. weigher. sintered Glass cruisible wash once by decantatn with 2 N-HCl, transfer the PPt to the cruisible & again wash with 2N-HCl followed by water.

4. dry to constant wt. at 100 – 105 °C or in a vaccume desicator.

Calculation :-

$$\% \text{ of purity of sample} = \frac{w \times F \times 100}{W}$$

w = wt. of 2,4-DNPH

F = Gravametric factor

W = wt. of the sample.

Determination of Nitrogroup by Reductn Method (or) Nitro, Nitraso & azo groups by Titanous salts (Reductn method)

Reagents

* Sample (Nitro, Nitraso group)
* Glacial acetic acid
* dil. H_2SO_4
* Titanous salts (Titanous sulphate or Titanous chlor
* Ammonia thio cyanide indicator (10%)

* Ammonium sulphate (fe (III))
* Steam of inert gas (CO_2 or N_2)

Preparatn

As described as azo group

Principle :-

The use of solutn of titanous chloride & of titanous sulphate for the quantitative reductn of selected organic compounds.

* Nitro groups are reduced to amines, the reactn is as follows

$$R-NO_2 + 6Ti^{3+} + 6H^+ \longrightarrow R-NH_2 + 6Ti^{4+} + 2H_2O.$$

* As well as Nitroso compounds are reduced to amines

$$R-NO + 4Ti^{3+} + 4H^+ \longrightarrow RNH_2 + 4Ti^{4+} + H_2O.$$

* The compound is dissolved in water, alcohol or acetic acid, & an excess of the soln of the titanous salt added
* After the reactn mixture has been boiled in a stream of inert gas (CO_2 or N_2)
* The excess of titanous salt is titrated with standard ferric ammonium sulphate (Fe III) soln, using Ammonium thio cyanate soln as indicator
* the NO_2 content of the sample can be calculated, six equivalence of the titanous salts are required for each nitro group
* Satisfactory results are obtained under the usual experimental condits with meta nitro aniline, P-nitro aniline, O-nitro Phenol, P-Nitro Phenol, M-dinitro benzene, 2,4-dinitro toulene, trinitro benzene

Picric acid, & 2,4-DNPH.

Procedure :

1. weigh out accurately a dry sample containing about 0.015 gms of Nitro group into the titratn flask, dissolve it in water or dil. Mineral Acid, If water insoluble prefer ethanol or Glacial acetic acid

2. Add 25 ml of dil. H_2SO_4, Pass CO_2 to the flask for 5 mins to remove oxygen

3. Add 50 ml of the 0.1 N titanous salt soln & boil for 5-10 mins (Attach a Reflex Condenser during the boiling period for volatile Samples)

4. Maintain the passage of inert gas, cool to 35-40°C add 10 ml of 10% Ammonium thio cynate soln & titrate with standard 0.1 N Fe(III) soln to a Pale Red end point.

Blank:

Carry out a Blank on 50 ml of the titanous sulphate soln

Calculatn:

% of purity of Nitrogroup: $$\frac{(V_1 - V_2) \times N_1 \times M \times 100}{w \times n \times 1000}$$

V_1 = Vol. of Fe(III) soln used for Blank

V_2 = " " sample

N_1 = Nor. of Fe(III) soln

M = m.wt of sample

w = wt. of sample

n = No. of nitro groups

$-NO_2 \cong 6\ Ti^{3+} \cong 6\ Fe^{3+}$

1 ml of 0.1 N $Ti^{3+} \cong$ 1 ml of 0.1 N $Fe^{3+} \cong$ 0.7669 mg of NO_2

Olefins (unsaturatn).

Reagents :-

1. Sample
2. Pottasium bromate Bromide soln
3. Hyp
4. Starch
5. 10% KI
6. 10% H_2SO_4
7. Mercuric sulphate/chloride.
8. Nacl
9. Carbon tetrachloride (CCl_4) - Solubility of Sample.

Preparation of Reagents

Preparatn of Mercuric sulphate/chloride (0.2 N)

Dissolve 15 gms of pure Mercuric sulphate in a soln prepared from 14 ml of conc. H_2SO_4 & 175 ml of H_2O

Preparatn of NaCl (2 N)

Dissolve 58.5 gms of AR-NaCl in 500 ml of distilled H_2O

Principle :-

The no. of double bonds in the compound may be calculated by brominatn.

* The Bromine liberated by acid from a standard soln of potassium Bromate & Bromide ep conducted in the presence of Mercuric Sulphate as a catalyst.

$$KBrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3Br_2 + 3K_2SO_4 + 3H_2O$$

* The excess of Bromine Calculated by addetion of KI

$$3Br_2 + 2KI \longrightarrow I_2 + 2KBr$$

* The liberated Iodine is titrated with standardised Hypo soln by using starch as Indicator.

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

* This procedure gives quantitative result for a limited no. of compounds (ex:- cyclohexene, 1-hexene, allyl alcohol, propionic acid & Malic acid)
* The determinatn of unsaturatn developed primarily for the analysis of animal & vegetable fats & oils unsaturatn values expressed by Iodine number or Bromine Number

Procedure :-

* Introduce a known amount of the sample into a 250 ml Iodine flask, & add a excess of the Bromate-Bromide soln & about 20 ml of 10% H_2SO_4

shake the flask for 5 mins & allow to stand for Bromine liberated

* & Add 10 ml of the mercuric sulphate soln & mix well, shaking for 7-10 mins then add 15 ml of 2N-NaCl soln, followed by 20 ml of 10% KI soln, shake the flask for about 30 sec; & titrate the liberated Iodine with standard 0.1N-Hypo soln, add about 0.5 ml of starch soln near the end point

Blank:

Run a blank determinatn with Bromate-Bromide soln used in the analysis, under the same experimental condetions like as sample.

Calculation:-

$$\% \text{ of purity of drug} = \frac{(V_1 - V_2)\, N_1 \times M \times 100}{w \times B \times 2000}$$

V_1 = Vol. of hypo consumed by blank

V_2 = Sample

N_1 = Nor. of hypo

w = wt. of sample

m = mol. wt of sample

B = No. of moles of Bromine absorbed by 1 mole of the compound-B determined.

Methoxy Group

Brominatn Method :-

Reagents :-

1. Sample
2. Bromine in sodium acetate, acetic acid
3. 10% H_2SO_4
4. formic acid
5. Hypo
6. starch
7. 10% KI

Preparatn of Reagents

1. Preparatn of Bromine in sodium acetate

Dissolve 10 gms of AR Anhydrous sodium acetate in 100 ml of Glacial acetic acid, add 3 ml of AR. Bromine per 10 ml of soln immediatly before use.

Principle :-

* The determinatn is based upon a procedure 1st suggested by S. Zeisel in 1885.
* A known wt. of the compound is decomposed by heating with constant boiling hydroiodic acid (HI) Yields the volitile methyl iodide.

$$R\text{-}OCH_3 + HI \longrightarrow CH_3I + R\text{-}OH$$

* the alkyl iodide is further oxidises to iodine mono bromide & iodic acid

$$CH_3I + Br_2 \longrightarrow \underset{\text{methyl bromide}}{CH_3Br} + IBr$$

~~$IBr + 2B$~~

~~$IBr + 2Br_2 + 3H_2O \longrightarrow HIO_3 + CH_3Br + IBr$~~

Iodine mono Bromide

$$IBr + 2Br_2 + 3H_2O \longrightarrow \underset{\text{Iodic acid.}}{HIO_3} + 5HBr$$

* Excess of Bromine is distroing with the formic acid

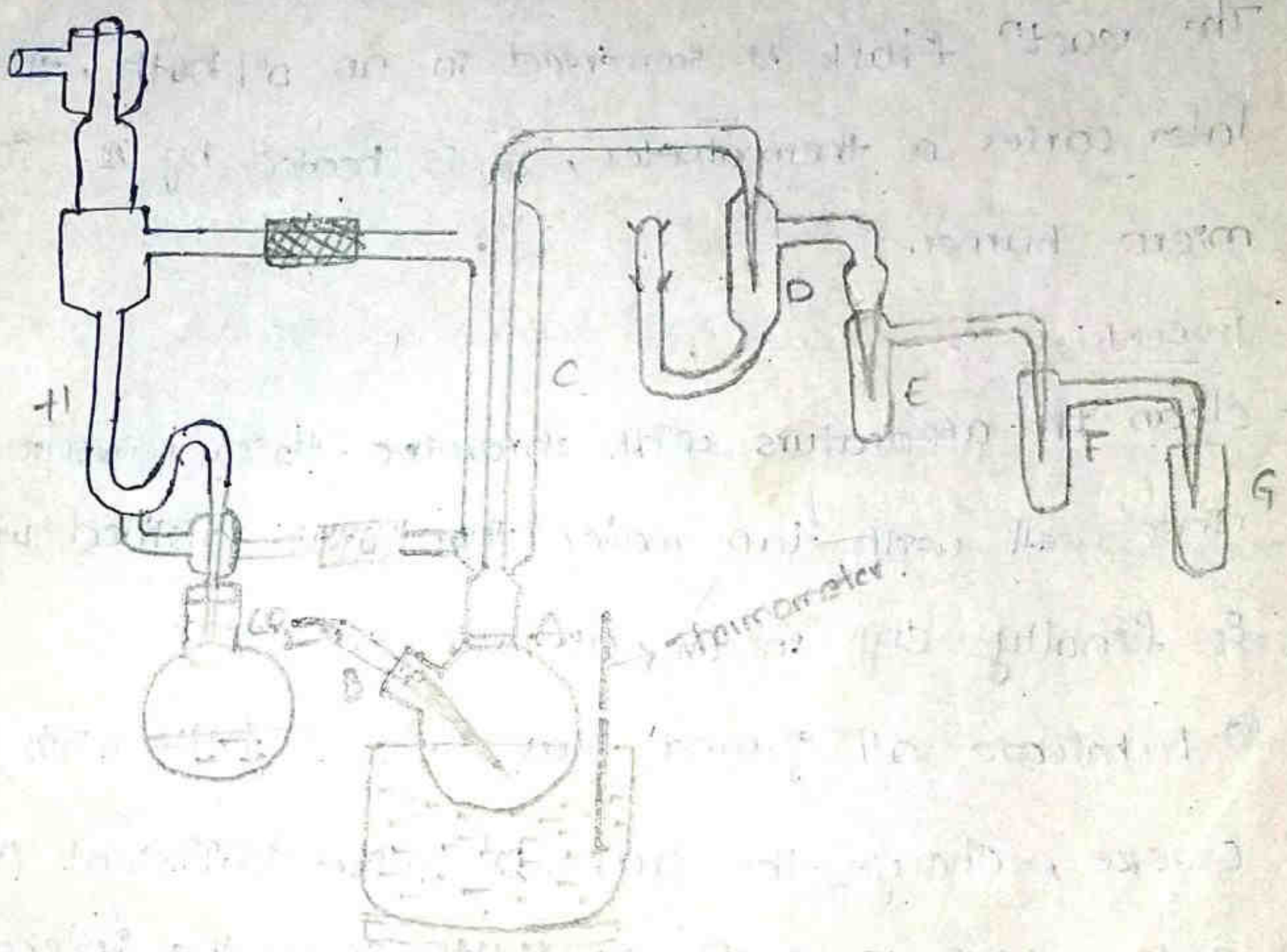
$$Br_2 + HCOOH \longrightarrow 2HBr + CO_2$$

* the liquid is then acidified with H_2SO_4, HI is added, & the liberated Iodine is titrated with standard hypo soln

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O.$$

$$3I_2 + 6NaS_2O_3 \longrightarrow 6NaI + 3Na_2S_4O_6$$

Apparatus :-



⇒ The apparatus consists of a pirets, two necked, round bottomed 100 ml flask A, B fitted with two standard glass joints

⇒ A Liebig condensor 'c' (14-15 cm Jacket) & trap the attached at 'A', the trap 'B' two test tube receiver

'E' & 'F', G is safty tube.

⇒ The tube 'G' serves to collect any liquid should be passage of gas through the apparatus accedentally fast

⇒ The capillary tubing pasing through the ground joint at 'B' is connected to a source of CO_2, 'H' is a devise by means of which the vapour of the liquid boiling in the flask can be passed through the condensor 'C'

⇒ The reactn flask is immersed in an oil bath, the later caries a thermometer, & is heated by a semi micro burner.

Procedure :-

1. Clean the apparatus with chromine - H_2SO_4 mixture. rinse well with tap water then with distiled water & finally dry in an air oven at 120°C
2. Lubricate all ground glass joints lightly with Silicon-Greeze, Charge the trap 'D' with Sufficient antimonyl sodium tartrate soln to just cover the internal tube. (The reagent have been used in the washer or scruber)
3. This reagent will effectively absorbe HI, Iodine & hydrogen sulphide but will not retain the alkyl iodide, place 10-10 ml of the CH_3COOH-sodium

acetate – Bromine soln in 'E' & equal volume in 'F'

4. weigh out accurately about 25 mg of solid sample. (methoxy group) into the reactn flask through 'B' disconect the flask for this purpose.

5. Add about HI, attach the flask to the Condensor 'C' Introduce, insert the capilary tube & Connect to the Source of CO_2 & heat the oil bath gradually

6. Adjust the rate of passage of CO_2 through the apparatus.

So that the rate of bubbling in the receivers 'E' & 'F' is under control, the temp of the oil Bath should reach 145°c in water bath

7. The reactn is then complete transfer the contents of the recivers 'E' & 'F' Quantitatively to a 250 ml flask fitted with a glass stoppered add AR- formic acid (90%) drop by drop to the soln in the titratn flask until the smell of Bromine can no longer be detected

8. Inert the stopper shake the flask well & cool it slightly

Dilute the soln to about 100 ml, add 1gm of AR- potassium iodide & 10 ml of 10% H_2SO_4 & allow to stand for 3-5 min

Titrate the liberated iodine with standard $Na_2S_2O_3$ soln using starch as indicator.

Blank :-

A Blank determinatn may be done run on the reagents under the same experimental conditn like of sample.

calculation :-

$$\% \text{ of Methoxy group} = \frac{V_1 \times N_1 \times M \times 100}{\omega \times 6 \times 1000}$$

V_1 = Vol. of sodium thiosulphate soln used for soln

N = Nor. of sodium thio sulphate

M = m.wt. of methoxy group

ω = wt. of sample

6 = No. of moles of sodium thio sulphate required

$R\text{-}OCH_3 \cong CH_3I \cong HIO_3 \cong 3I_2 \cong 6 Na_2S_2O_3$.