EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. IR spectra were recorded in KBr/Nujol/neat on a IR-408 Shimadzu spectrophotometer. $^1$H-NMR were determined on Hitachi Perkin Elmer (80 MHz) instrument in CDCl$_3$ using TMS as internal standard, and chemical shifts recorded in $\delta$ values relative to TMS assigned at zero. The refractive indices were measured on Abbe refractometer using visible light (electric bulb) with temperature maintained at 20-25 °C. Slight deviations in the observed values in relation to the reported ones are thus explained.

The Gas chromatograms were determined on a Nucon Gas Chromatograph using a glass column of carbowax-200 C maintaining the oven temperature above the boiling point of the aldehydes. TLC were carried on silica gel G$_{254}$ (E. Merck). Iodine or 2,4-dinitrophenylhydrazine were used for visualization of TLC plates.

The aldehydic reagents - Tollens', Fehling's and Benedict's used for testing prepared aldehydes were of Analytical reagent grade (BDH or Qualigen).
**General experimental procedure - Preparation of acid chlorides**

The acid chlorides were prepared by standard methods from the corresponding acids. The acid (0.1 M) was dissolved in benzene or chloroform (20 ml) and to this thionyl chloride (0.15 M) added. Where required dimethylformamide was used as a catalyst. The mixture was refluxed for varying degrees of time till the evolution of HCl ceased. The solvent was evaporated to give the acid chloride which was distilled before used.

**Derivatisation**

**Phenylhydrazone** - Phenylhydrazine hydrochloride solution was prepared by dissolving phenylhydrazine in ethanol and concentrated HCl added to it. The solid phenylhydrazine hydrochloride obtained thus was crystallised. Phenylhydrazine hydrochloride (5 gm) and sodium acetate (8 gm) were dissolved in water (50 ml) to obtain a stock solution. To an aliquot of this solution an alcoholic solution of the aldehyde was added and stirred till a clear solution was obtained. The whole mixture was warmed on water bath for 20 minutes, cooled and filtered to obtain a solid which was crystallised from ethanol.

**2.4 - Dinitrophenylhydrazone** - To the clear solution obtained by warming 2.4-dinitrophenylhydrazine, HCl (1 ml) and ethanol (8-10 ml) the aldehydic solution was added and the mixture heated to boil. This
mixture was cooled and filtered to obtain the solid 2,4-dinitrophenylhydrazone which was crystallised from ethanol.

**General experimental procedure for aldehyde synthesis:**

The prepared acid chloride (3-5 gm) was dissolved in chloroform (15 ml) and the solution deoxygenated by bubbling \( \text{N}_2 \) through the solution. This solution was covered by ammonium hydroxide (25%) followed by gradual addition of formic acid (excess: three fold over acid chloride), the whole mixture being stirred for varying degrees of time under \( \text{N}_2 \). The reaction was monitored on the basis of evolution of \( \text{CO}_2 \). When the \( \text{CO}_2 \) evolution ceased, the reaction mixture was stirred for another 5 minutes. The organic layer was separated washed with water and dried over anhydrous sodium sulphate (\( \text{Na}_2 \text{SO}_4 \)). The product was obtained by evaporating the solvent under nitrogen to prevent the possible aerie! oxidation of aldehyde formed.

**Tests for Aldehydes**

I. **Tollens' Test** - 2 ml of Tollens' reagent along with few drops of isolate was shaken well and heated on a water bath. A silver - mirror or a greyish black ppt confirmed the presence of the aldehyde function.

II. **Fehling's Test** - 1ml of isolated solution together with 2 ml of freshly prepared Fehling's solution obtained by mixing 1 ml of Fehling's solution A with 1 ml of Fehling's solution B was warmed. A positive response was indicated by the appearance of a red precipitate.
111. **Benedict's Test** - 5 ml of Benedict's reagent along with 0.5 ml of isolated solution was heated together directly on a flame. A red/yellow/green colour indicated a positive response.

**Benzaldehyde**

1. **Reactants**: Benzoyl Chloride (4 gm; 0.028 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (4.6 gm; 0.1 M), reaction time 50 minutes, Yield 79%
   - Tollens' test : Positive
   - Fehling's test : Negative
   - Benedict's test : Positive
   - Refractive index : 1.522
   - Phenylhydrazone mp : 156 - 58°C
   - 2,4-Dinitrophenylhydrazone mp : 235 - 39°C
   - GLC (Solvent: chloroform) : Retention time 4 minutes
   - IR (KBr) $\nu_{\text{max}}$ : 1705 cm$^{-1}$ (C=O)
   - $^1$H-NMR (CDCl$_3$) : $\delta$ 7.5 (m, 3H), 7.75 (m, 2H), 9.95 (s, 1H)

2. **Reactants**: Benzoyl Chloride (4 gm; 0.028 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), sodium formate (6.8 gm; 0.1 M) in distilled water (5 ml): reaction time 50 minutes, Yield 75%
   - Tollens' test : Positive
   - Fehling's test : Negative
Benedict's test : Positive
Refractive index : 1.522

Phenylhydrazone mp : 156 - 58°C
2,4- Dinitrophenylhydrazone mp : 235 - 39°C

GLC (Solvent; chloroform) : Retention time 4 minutes

3. Reactants: Benzoyl Chloride (4 gm: 0.028 M) in chloroform (15 ml), 0.3 M sodium hydroxide aqueous solution (30 ml) formic acid (4.6 gm; 0.1 M): reaction time 30 minutes, Yield 72%

  Tollens' test : Positive
  Fehling's test : Negative
  Benedict's test : Positive
  Refractive index : 1.522
  Phenylhydrazone mp : 156 - 58°C
  2,4- Dinitrophenylhydrazone mp : 235 - 39°C
  GLC (Solvent: chloroform) : Retention time 4 minutes

Propionaldehyde

Reactants: Propionoyl chloride (3 gm: 0.033 M) in diethylether (15 ml): ammonium hydroxide (25%; 30 ml), formic acid (4.6 gm : 0.1 M) : reaction time 45 minutes, yield 79%

  Tollens' test : Positive
  Fehling's test : Positive
  Benedict's test : Negative
Refractive index  :  1.376

2.4 - Dinitrophenylhydrazone mp : 152 - 56°C

GLC (Neat) : Retention time 1.8 minutes

IR (KBr) $v_{\text{max}}$ : 1710 cm$^{-1}$ (C=O)

$^1$H-NMR (CDCl$_3$) : $\delta$ 10.1 (1H.s), 2.7 (2H.t), 1.6 (2H.m), 0.97 (3H.t)

**Butyraldehyde**

**Reactants** : Butyryl chloride (3 gm; 0.028 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (4.6 gm; 0.1 M);

reaction time 35 minutes, yield 90%.

- Tollens' test : positive
- Fehling's test : positive
- Benedict's test : Negative

Refractive index : 1.411

2.4 - Dinitrophenylhydrazone mp : 118 -24°C.

GLC (solvent : CHCl$_3$) : Retention time 6.12 minutes

**Phenylacetaldehyde**

**Reactants** : Phenylacetyl chloride (5 gm : 0.032 M) in chloroform (15 ml), ammonium hydroxide (25% : 30 ml), formic acid (4.6 gm : 0.1 M);

reaction time 50 minutes, yield 80%.

- Tollens' test : Positive
- Fehling's test : Positive
Benedict's test: Positive
Refractive index: 1.536

2.4-Dinitrophenylhydrazone mp: 126-28°C.

GLC (solvent: CHCl₃): Retention time 3.68 minutes

Isobutyraldehyde

Reactants: Isobutyryl chloride (4 gm; 0.037 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (5.32 gm; 0.12 M), reaction time 25 minutes, yield 86%.

Tollens' test: Positive
Fehling's test: Positive
Benedict's test: Positive
Refractive index: 1.401

2.4-Dinitrophenylhydrazone m.p.: 188-92°C

GLC (solvent: CHCl₃): Retention time 4.72 minutes.

Pivalaldehyde

Reactants: Pivaloyl chloride (4 gm: 0.033 M) in chloroform (15 ml), ammonium hydroxide (25%: 30 ml), formic acid (4.6 gm: 0.1 M), reaction time 20 minutes, yield 85%.

Tollens' test: Positive
Fehling's test: Positive
Benedict's test: Positive
Refractive index: 1.398
2.4-Dinitrophenylhydrazone (mp.): 207-211°C

**Monochloroacetaldehyde**

**Reactants**: Chloroacetyl chloride (4 gm; 0.035 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (4.6 gm; 0.1 M); reaction time 45 minutes, yield 82%.

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Positive
- Refractive index: 1.435
- 2,4-Dinitrophenylhydrazone mp: 108-110°C
- GLC (solvent: CHCl₃): Retention time 4.2 minutes.

**2-Chloropropionaldehyde**

**Reactants**: 2-chloropropionoyl chloride (4 gm; 0.031 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (4.6 gm; 0.1 M); reaction time 45 minutes, yield 79%.

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Negative
- Refractive index: 1.441
- 2,4-Dinitrophenylhydrazone mp: 137°C decomp.
- GLC (solvent: CHCl₃): Retention time 6.8 minutes.
**Trichloroacetaldehyde**

**Reactants**: Trichloroacetyl chloride (4 gm, 0.022 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (3.25 gm: 0.07 M); reaction time 50 minutes; yield 76% as trichloroacetaldehyde and chloralhydrate.

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Positive
- Refractive index: 1.449
- 2,4-Dinitrophenylhydrazone mp: 130-34 °C
- GLC (solvent: CHCl₃): Retention time 2.28 minutes.
- Chloralhydrate mp: 53 °C

**Lauraldehyde**

**Reactants**: Lauroyl chloride (4 gm: 0.018 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (2.75 gm: 0.06 M); reaction time 25 minutes, m.p. 43-46 °C. Yield 96%

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Positive
- 2,4-Dinitrophenylhydrazone mp: 104-108 °C
- TLC (silica-gel: G₂₅₄) Solvent: Petroleum ether: Ethylacetate: Acetic acid (70: 30: 1); $R_f = 0.08$
**Palmaldehyde**

**Reactants**: Palmitic acid chloride (4 gm; 0.014 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (1.9 gm; 0.042 M); reaction time 20 minutes; mp 35°C, yield 95%

- Tollens' test : Positive
- Fehling's test : Positive
- Benedict's test : Positive
- 2,4-Dinitrophenylhydrazone mp : 107-110 °C
- TLC (silica gel : G254) Solvent : Petroleum ether : Ethylacetate : Acetic acid (70 : 30 : 1); Rf = 0.073

**Stearaldehyde**

**Reactants**: Stearic acid chloride (4 gm; 0.013 M) in chloroform (15 ml); ammonium hydroxide (25%; 30 ml), formic acid (1.9 gm; 0.042 M); reaction time 20 minutes. mp 57°C. yield 94%

- Tollens' test : Positive
- Fehling's test : Positive
- Benedict's test : Positive
- 2,4-Dinitrophenylhydrazone mp : 124-127 °C
- TLC (silica gel : G254) Solvent : Petroleum ether : Ethylacetate : Acetic acid (70 : 30 : 1); Rf = 0.65
**Olealdehyde**

**Reactants**: Oleoyl chloride (4 gm; 0.013 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (1.9 gm; 0.042 M)

reaction time 30 minutes, yield 91%

Tollens' test : Positive
Fehling's test : Positive
Benedict's test : Negative
Refractive index : 1.456

2,4-Dinitrophenylhydrazone mp : 67-70 °C

TLC (silicagel : G254) Solvent : Petroleum ether : Ethylacetate :

Acetic acid (70 : 30 : 1): $R_f = 0.58$

**10-Undecenaldehyde**

**Reactants**: 10-undecenoyl chloride (4 gm; 0.018 M) in chloroform (15 ml). ammonium hydroxide (25%; 30 ml). formic acid (2.75 gm; 0.06 M); reaction time 30 minutes. yield 91%

Tollens' test : Positive
Fehling's test : Positive
Benedict's test : Negative
Refractive index : 1.416

2,4-Dinitrophenylhydrazone mp : 132-35 °C

TLC (silicagel : G254) Solvent : Petroleum ether : Ethylacetate :

Acetic acid (70 : 30 : 1): $R_f = 0.50$
**Cinnamaldehyde**

**Reactants**: Cinnamoyl chloride (3 gm; 0.018 M) in chloroform (15 ml), ammonium hydroxide (25 %; 30 ml), formic acid (2.5 gm; 0.054 M); reaction time 50 minutes. yield 90%

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Positive
- Refractive index: 1.621
- 2,4-Dinitrophenylhydrazone mp: 202-205 °C
- GLC (solvent: CHCl₃): Retention time 2.95 minutes.

**3,3-Dimethylacraldehyde**

**Reactants**: Dimethylacroyl chloride (5 gm; 0.042 M) in chloroform (15 ml), ammonium hydroxide (25 %; 30 ml), formic acid (6.0 gm; 0.13 M); reaction time 45 minutes. yield 86%

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Positive
- Refractive index: 1.457
- 2,4-Dinitrophenylhydrazone mp: 155-58 °C
- GLC (solvent: CHCl₃): Retention time 2.2 minutes.
Phenylpropiolaldehyde

Reactants: Phenylpropionic acid chloride (3 gm; 0.018 M) in chloroform (15 ml), ammonium hydroxide (25%; 30 ml), formic acid (2.5 gm; 0.054 M); reaction time 50 minutes, yield 79%

- Tollens' test: Positive
- Fehling's test: Positive
- Benedict's test: Positive
- Refractive index: 1.599
- 2,4-Dinitrophenylhydrazone mp: 188-90 °C

CATALYTIC TRANSFER HYDROGENATION

Preparation of precipitated-metal catalyst: ppt-Ni and ppt-Cu

Zinc dust (10 gm) and distilled water (3 ml) were placed in an Erlenmeyer flask and heated on water bath. An aqueous solution (10 ml) containing either 4.04 gm of nickel(II) chloride (NiCl₂.6H₂O) or 2.69 gm of copper(II) chloride (CuCl₂.6H₂O), previously heated to 60 °C, was added to the heated zinc dust mud with vigorous shaking. A violent reaction took place, depositing the Ni or Cu on the surface of the zinc dust. The whole solid was collected on a glass filter by suction, washed with water three times and then with methanol and ether and dried under reduced pressure. The precipitated metal catalyst obtained thus contains about 1 gm of each metal, supported on zinc dust.
**General Reduction procedure**

Formic acid and excess trimethylamine were taken and to this, the solution of acid chloride in benzene (10 ml) added. The molar ratio of formic acid and acid chloride taken were 4:1. Temperature of the mixture was maintained at room temperature by cooling. 1 gm each of the ppt metal catalyst of either Ni or Cu was added to the above solution with continuous stirring, when a vigorous reaction took place with the effervescence. After evolution of the gas had ceased, the reaction mixture was heated on water bath for varying degrees of time. The catalyst was filtered and the filtrate washed with water and dried over anhydrous sodium sulphate (Na$_2$SO$_4$). An alcoholic solution of 2,4-dinitrophenylhydrazine hydrochloride was added to the benzene solution and 2-4-dinitrophenylhydrazone formed was filtered, dried and crystallized from ethanol. Yields were calculated on the basis of the phenylhydrazone formed.

**Benzaldehyde**

**Reactants:** Benzoyl chloride (2 gm: 0.014 M) in benzene (10 ml). formic acid (2.76 gm, 0.06 M). trimethylamine (4 ml). ppt-Ni or ppt-Cu catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1 hour: Yield 73% and for ppt-Cu catalyst: 1.5 hours. Yield 76%

2,4-Dinitrophenylhydrazone mp : 235-38 °C.
Butyraldehyde

Reactants: Butyryl chloride (2 gm; 0.019 M) in benzene (10 ml), formic acid (3.70 gm; 0.08 M), trimethylamine (4 ml). ppt-Ni or ppt-Cu catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1 hour, yield 66% and for ppt-Cu catalyst: 1.5 hours, yield 70%.

2,4-Dinitrophenylhydrazone mp: 120-5°C.

Isobutyraldehyde

Reactants: Isobutyryl chloride (2 gm; 0.019 M) in benzene (10 ml), formic acid (3.70 gm; 0.08 M), trimethylamine (4 ml). ppt-Ni or ppt-Cu catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1.5 hours, yield 75% and for ppt-Cu catalyst: 2 hours, yield 77%.

2,4-Dinitrophenylhydrazone mp: 186-90°C.

Pivalaldehyde

Reactants: Pivaloyl chloride (2 gm; 0.016 M) in benzene (10 ml); formic acid (3.22 gm; 0.07 M), trimethylamine (4 ml). ppt-Ni or ppt-Cu catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1.5 hours, yield 77% and for ppt-Cu catalyst: 2 hours, yield 81%.

2,4-Dinitrophenylhydrazone mp: 204-208°C.

Stearaldehyde

Reactants: Stearic acid chloride (2 gm; 0.006 M) in benzene (10 ml). formic acid (1.38 gm; 0.03 M), trimethylamine (4 ml). ppt-Ni or ppt-Cu
catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1 hour, yield 81% and for ppt-Cu catalyst: 2 hours, yield 87%.

2.4 - Dinitrophenylhydrazone mp: 123-27°C.

**Reduction of Oleoyl chloride**

**Reactants**: Oleoyl chloride (2 gm: 0.006 M) in benzene (10 ml), formic acid (1.38 gm: 0.03 M), trimethylamine (4 ml), ppt-Ni or ppt-Cu catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1 hour, yield 83% and for ppt-Cu catalyst: 2 hours, yield 74%.

2.4 - Dinitrophenylhydrazone mp: 125-7°C.

**Reduction of Cinnamoyl chloride**

**Reactants**: Cinnamoyl chloride (2 gm: 0.012 M) in benzene (10 ml), formic acid (2.76 gm: 0.06 M), trimethylamine (4 ml), ppt-Ni or ppt-Cu catalyst (1 gm). Reaction time for ppt-Ni catalyst: 1 hour, yield 78% and for ppt-Cu catalyst: 2 hours, yield 73%.

2.4 - Dinitrophenylhydrazone mp: 150-54°C.