

## Appendix - I

### Preparation of olefins:

I. Cyclohexene<sup>1</sup> from cyclohexanol: In a 500 ml distn flask, 400 gms of cyclohexanol and 10 ml conc. sulphuric acid were well mixed and 2-3 pieces of porous chip were added. The flask was set for distillation with a good condenser and a receiver surrounded by an ice bath. The contents of the flask was heated in an oil bath to a temperature of  $130^{\circ}$ - $140^{\circ}$  C. The distillation began and distillate was collected in the receiver until only a small residue remained behind and the odour of sulphur dioxide was apparent. Toward the end of the distillation the temperature of the oil bath might be allowed to rise slowly to  $150^{\circ}$  C. The distillate was transferred to a separatory funnel, saturated with brine solution, washed successively with 5% sodium bicarbonate solution and water. The cyclohexene was separated from the water layer and dried over anh. calcium chloride. Now the crude product was distilled where by a fraction of b.p.  $80$ - $82^{\circ}$  C was collected in a dry receiver. It was redistilled b.p. =  $80$ - $81^{\circ}$  C. Yield = 246 gms (75%).

II. Preparation of Cyclohexene-2-one<sup>2</sup>: (a) Ketallization of Cyclohexanone: In a 1 litre flask 100 gms (1.04 mol) of cyclohexanone, 500 ml of dry benzene and 70.0 gms (1.125 mol) of ethylene glycol were well mixed together and catalytic amount of p-toluene sulphonic acid was added. The flask was fitted with a Dean-Stark apparatus and refluxed for 6 hrs.

Solvent benzene was removed completely and the liquid residue washed successively with 5% sodium bicarbonate solution and water, dried over anh. sodium sulphate. The crude cyclohexane dimethyl ketal was purified by distillation under reduced pressure, b.p. = 140-145<sup>o</sup> C/5 mm. Hg., yield = 115 gms (80%).

(b) Bromination of Cyclohexane dimethyl ketal : To a stirred solution of 115 gms (0.61 mol) of ketal product in a 1 litre anh. methanol, taken in a 2 litre three necked flask, was added a small portion of bromine. The flask was now surrounded by ice water bath. When the uptake of bromine began the remainder of 128 gms of bromine was added dropwise at 15-20<sup>o</sup> C. Solvent methanol was removed completely at room temperature and the residue was treated with brine solution to remove hydrogen bromide, and dried over anh. sodium sulphate. Yield = 139 gms (62%).

(c) Dehydrobromination of Bromo ketal derivative of Cyclohexane: In a 500 ml r.b. flask, 67.0 gms (0.30 mol) of bromoketal product was treated with a solution of 48.0 gms of sodium methoxide in 150 ml dry dimethyl sulphoxide. When the reaction set in, it was cooled under water bath so that the temperature remained below 30<sup>o</sup> C. After the reaction had subsided, the reaction mixture was left at room temperature for five hrs. Now the reaction mixture was poured into one litre portion of water. It was then saturated with sodium chloride salt and the product was extracted with two

500 ml portion of n-hexane. The extract was dried over anh. sodium sulphate. Now solvent was removed on the water bath and the liquid residue was distilled under reduced pressure to afford Cyclohexanone dimethyl ketal-2-one. B.p. = 130-135 °C/5 mm. Hg. (approximate), yield = 32.0 gms (75%).

(d) Dehydration of Cyclohexanone dimethyl ketal-2-one : 32.0 gms of the above dimethyl product was placed in a 100 ml separatory funnel and 30 ml of 3% aqueous sulphuric acid solution was added and shaken vigorously for 30 minutes. The acidified solution was allowed to stand overnight and extracted several times with ether. The combined extracts were washed with 5% sodium bicarbonate solution, and dried over anh. sodium sulphate. Solvent ether was removed completely and the residue distilled at low pressure under vacuum; b.p. = 120-125 °C/5 mm. Hg. (approximately), yield = 20.0 gms (90%).

III. Preparation of 1-acetyl Cyclohexane<sup>3</sup> : In a 1 litre three necked flask, fitted with a condenser topped with anhydrous calcium chloride guard tube, a mixture of cyclohexane and 1 mole of acetyl chloride in 500 ml dry carbon disulphide was placed and the mixture was stirred vigorously. Now 1.2 mole of anhydrous aluminium chloride was added in a small portion to stirred mixture for a period of 2 hrs. After addition, the mixture was continuously stirred for 8 hrs. between 50-70 °C. The complex salt was decomposed by mineral acid, washed and the carbon disulphide extract was dried over anh. calcium chloride. Now the solvent carbon disulphide was

was distilled off and the liquid reaction product was distilled under reduced pressure to separate the lower boiling 2-chloro ketone, subsequently the higher boiling required product; Yield = 66.0 gms (37%).

IV. Preparation of 1, 2-dihydro naphthalene<sup>4</sup>: (a) Sodium borohydride reduction of -tetralone:

55 gms of -tetralone was dissolved in 200 ml of dry methanol taken in a 500 ml three necked flask, fitted with a condenser. Now 20 gms (0.54 mole) of anh. solid sodium borohydride was added to the stirred solution of -tetralone in a small amount at such a rate that mild refluxing occurred. After addition of borohydride, the reaction mixture was continuously stirred for 2 hrs. and then allowed to stand overnight at room temperature. Solvent methanol was removed completely by slow heating of the reaction mixture on water bath while the solid residue left behind was decomposed by 3 N hydrochloric acid solution in cold. The reaction mixture saturated with brine solution, was extracted with 100 ml of ether twice. Ether extract was now washed twice with saturated brine solution and dried over anh. sodium sulphate. Solvent ether was removed completely whereby almost colourless liquid residue was left behind in the flask. Yield = 45.0 gms. (81%).

(b) Dehydration of 1-hydroxy-1,2,3,4-tetrahydronaphthalene: The above crude liquid product (45 gms) was taken in a 250 ml dry r.b.

flask and treated with 60 ml of dry ortho phosphoric acid with vigorous shaking. The reaction mixture was then heated gently on water bath for 1.5 hrs. and kept overnight at room temperature. The reaction mixture was poured into 200 ml cold water and extracted with 100 ml of ether twice. Ether layer was then washed successively with 5% sodium bicarbonate solution and water; and dried over anhydrous sodium sulphate. Ether was removed on water bath and the liquid residue left was distilled under reduced pressure : b.p. = 120-125°C/3 mm Hg. (approx.) Yield = 30 gms. (76%).

#### Preparation of Catalysts:

##### I. Active Copper powder<sup>5</sup> :

10.0 gms of recrystallised copper sulphate was dissolved in 35 ml of hot water in a 250 ml beaker with the help of a mechanical stirrer. After cooling to room temp. ; 3.5 gms (or more if necessary) of high grade zinc dust was added slowly with vigorous stirring until the solution decolorized. The brown ppt. of copper was washed by decantation with water. Now an aqueous solution of hydrochloric acid (5%) was added to the precipitate in order to remove the excess of unreacted zinc and stirring was continued till the evolution of hydrogen gas ceased. The copper powder was filtered, washed with water and kept in moist condition (as a paste) in a stoppered bottle.

II. Bis nickel<sup>II</sup> acetylacetonate<sup>6</sup> :

To a stirred solution of 23.75 gms (0.1 mol) of hydrated Nickel chloride in 100 ml water was added a solution of 20.0 gms of acetylacetonone (0.20 mol) in 60 ml methanol with constant stirring. To the resulting mixture a solution of 18.5 gm (0.20 mol) of sodium acetate in 60 ml of water was added while the mixture was heated gently on a hot plate. It was then cooled in the refrigerator for several hrs. The green solid was filtered on a buchner funnel, washed with water and dried in air. A needle shaped crystals (green) on recrystallisation from methanol was obtained.

III. Bis copper<sup>II</sup> acetylacetonate<sup>7</sup> :

17.0 gms of cupric chloride dihydrate was dissolved in 150 ml of water. Now 20.0 gms of acetyl acetone was added gradually with stirring. The solution turned deep blue and the solid product began to rise to the surface. The mixture was stirred continuously for 3 hrs. and allowed to stand overnight. The dark blue crystalline product was filtered, washed with water and dried in air. Recrystallisation of this product from chloroform gave mats of blue crystals; m.p. = 234.5°C (Lit. 236°C) Yield = 7.0 gms.

IV. Copper<sup>I</sup> chloride<sup>8</sup> :

In a 250 ml beaker, 12.5 gms of hydrated copper<sup>II</sup> sulphate and 3.2 gms of sodium chloride were dissolved in 50 ml hot water. Now an alkaline solution sodium sulphite (prepared from 2.6 gms of sodium bisulphite and 1.8 gms of sodium hydroxide dissolved in

20 ml water) was added gradually to the resulting hot solution with constant stirring. When the colour of reaction mixture disappeared or nearly so, it was cooled to room temp. and the supernatant liquid was decanted from the white ppt. of cuprous chloride. The precipitate was washed several times by decantation with dilute sulphurous acid solution to prevent aerial oxidation. It was then filtered, washed with small portion of glacial acetic acid, and dried in an evaporating dish until the odour of acetic acid is removed. The white cuprous chloride was stored in an air-tight stoppered bottle.

Preparation of allyl magnesium bromide:

In a 250 ml three necked flask, fitted with a stirrer, a dropping funnel and a good condenser, 5.0 gms (0.208 gm. atom) of cleaned magnesium turning in 50 ml of anh. ether was taken. A solution of 12.0 gms (0.1 mol) of allyl bromide in 100 ml dry ether was added a small portion until reaction began and then rate of addition was adjusted in such a manner so as to maintain gentle refluxing. The addition required 1.5 hr, after which the reaction mixture was refluxed gently and stirred for an additional 2 hrs. Thus an ethereal solution of allyl magnesium bromide was prepared and kept in cold condition for subsequent reactions.

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## Appendix - II

### Some other references

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