

## CHAPTER - II

### Experimental

#### N-Cyclohexylhydroxylamine:

Pyridine hydrochloride was prepared by passing dry hydrogen chloride through a solution of dry and distilled pyridine in dry ether till precipitation of pyridine hydrochloride was complete. The precipitate was quickly filtered and dried under vacuum.

To a solution of pyridine hydrochloride (65.9 g, 0.57 mole) suspended in dry pyridine (150 ml.), a solution of sodium borohydride (22.14 g, 0.565 mole) in dry pyridine (375 ml.) was added dropwise under nitrogen atmosphere and perfectly anhydrous condition, when sodium chloride precipitated. The reaction mixture was filtered quickly through a sintered glass filter under suction and anhydrous condition and the filtrate was concentrated at 30° under vacuum (5 mm/Hg), when pyridine-borane remained in the flask as a pale yellow liquid (49 g, 93%). The reagent was used in the next step without further purification.

A mixture of cyclohexanone oxime (5.6 g, 0.05 mole) and pyridine-borane (25 ml., 0.25 mole) in ethanol (25 ml.) was kept at 5° with stirring for 30 min. To this solution 10% hydrochloric acid (50 ml.) was added dropwise and the

mixture was stirred at room temperature for 30 min more. The solution was then made alkaline with saturated sodium bicarbonate solution and extracted with benzene (25 ml. x 3). The combined benzene extracts were washed with water (25 ml. x 3) and dried over anhydrous magnesium sulphate. On removal of benzene  $\beta$ -cyclohexylhydroxylamine was obtained as a white solid residue (5.2 g, 91%), m.p.  $137^{\circ}$ . This was crystallised from ethanol to obtain white needles, m.p.  $140^{\circ}$ . Mixed melting point with the authentic sample showed no depression.

IR (Nujol):

3220s, 3140(b)s, 1530s, 1345m, 1310m, 1275w,  
1250w, 1210s, 1150s, 1120m, 1080s, 1065s, 1035s, 975s,  
930s, 910s, 890s, 840s, 790s, 570m, 500s.

$\alpha$ -Amino- $\beta$ -cyclohexyl nitrene (XXII):

$\beta$ -Cyclohexylhydroxylamine (1g, 8.7 m moles) was added to freshly distilled dry formamide (25 ml. ) in a 100 ml round-bottomed flask fitted with a calcium chloride guard-tube and a nitrogen balloon. The flask was kept at  $5^{\circ}$  and anhydrous magnesium sulphate was added, which settled at the bottom, whereas sparingly soluble and light  $\beta$ -cyclohexylhydroxylamine floated on the surface of formamide.

The mixture was then stirred at 5° for 3 hrs. when N-cyclohexylhydroxylamine went into solution due to the formation of the nitrene (XXXI). The reaction mixture was kept at 5° for 16 hrs. more and then filtered. The filtrate was taken in ether (75 ml.) and washed with water (25 ml. x 4) to remove formamide. The ether layer was dried over anhydrous magnesium sulphate and concentrated under vacuum to furnish the nitrene (XXXI) as a white solid (0.52 g) showing a strong characteristic peak at 1620 cm<sup>-1</sup> in the IR. Further characterization through crystallization could not be done, as the nitrene decomposed on keeping. The nitrene was therefore generated in formamide by the above method and used in situ for further reactions.

IR (Nujol):

3400 - 3250(b)s, 1830s, 1600w, 1390s, 1340w, 790w.

Reaction of (XXXI) with benzyl chloride:

To a solution of the nitrene (XXXI) generated from N-cyclohexylhydroxylamine (2g, 17.39 m mole) in formamide (50 ml.) by the above method and filtered carefully under anhydrous condition and nitrogen atmosphere from the magnesium sulphate through a sintered glass filter under suction, was added freshly distilled benzyl chloride (2.2g,

17.4 mmole). Benzyl chloride was sparingly soluble in formamide; but on stirring at room temperature for 9 hrs. it gradually went into solution due to formation of (XXXII) which gave a characteristic spot in the TLC. The solution was used in the next step without further characterization.

TLC : Benzene : Ethyl Acetate = 19:1

Single spot,  $R_f = 0.628$

Formation of benzaldehyde:

To the above solution of (XXXII) in formamide powdered sodium carbonate (2 g) was added and the mixture was stirred under nitrogen atmosphere for 9 hours at room temperature, when the formation of benzaldehyde was observed by careful comparative TLC studies.

TLC : Benzene : Ethyl Acetate = 10:1

$R_f = 0.91$

The above reaction mixture was poured into ether (150 ml.) and washed with water (50 ml x 4) to remove formamide. Usual work up furnished a pale yellow liquid which probably contained, apart from benzaldehyde, the condensation product (XXXV). The reaction mixture was hydrolysed in the following way.

To the above reaction mixture 50% aqueous methanolic hydrochloric acid (15 ml.) was added and the resulting solution was refluxed for 3 hrs. under nitrogen atmosphere. Usual work up furnished benzaldehyde (0.25 g) which was distilled in <sup>a</sup> bulb tube and characterized by TLC and IR and through formation of NPH (m.p. 237°). Mixed melting point with the NPH of an authentic sample of benzaldehyde showed no depression.

TLC:

Benzene : Ethyl Acetate = 19:1

Single spot,  $R_f = 0.91$

Chromatographic Separation of (XXXVII):

A mixture containing mainly (XXXIV) and (XXIV) (0.5 g) from another experiment was chromatographed over a column of aluminium oxide (50g) deactivated by adding 10% water. The major fraction (0.33 g) was eluted with petroleum ether (60° - 80°). This fraction showed a single spot in the TLC and was characterized to be (XXXVII) by IR.

TLC:

Benzene : Ethyl Acetate = 19:1

$R_f = 0.49$

IR (film):

3300(b)s, 3063w, 3020w, 2920s, 2840s, 1870w,  
1810w, 1750w, 1660s, 1630m, 1490m, 1450s, 1350s, 1320s,  
1300s, 1250s, 1220s, 1160w, 1150s, 1100m, 1030m, 1020m,  
980s, 960w, 930m, 920m, 900s, 840m, 800w, 780s, 750m,  
700s.

Hydrolysis of (XIVII) to benzaldehyde:

The above product (0.28 g) was hydrolyzed by 50% aqueous methanolic hydrochloric acid (15 ml.) under reflux for 3 hrs under nitrogen atmosphere and worked up as usual with ether, when benzaldehyde was obtained which was characterized by formation of DNPH.

R E F E R E N C E S

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