

CHAPTER III

EXPERIMENTAL

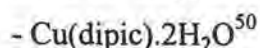
Instrumentation

Melting points were determined with a John-Fisher melting point and are uncorrected. FTIR spectra were recorded on Nicolet model Impact 410. ^1H and ^{13}C -NMR spectra were performed in deuteriochloroform with tetramethylsilane (TMS) as an internal reference on a Bruker Fourier Transform NMR Spectrometer ACF 200 Mhz. Gas chromatography analysis was carried out on a Shimadzu gas chromatograph GC-9A instrument equipped with flame ionization detector (FID) with N_2 as a carrier gas. The column used for chromatography was carbowax 20M.

Chemicals

Chemicals were purchased from Fluka Chemical, Co. Copper salts such as cupric acetate monohydrate, cupric chloride, cuprous chloride, *etc.* were purchased from Fluka Chemical, Co. Hydrogen peroxide 30% in water was obtained from Carlo Erba Reagent. Solvents were used as purchased.

Preparation of Copper Complexes and Authentic Specimen



Cupric acetate monohydrate (4.0 g, 20.1 mmol) and pyridine-2,6-dicarboxylic acid (3.4 g, 20.1 mmol) were heated to boiling in 175 mL of distilled water. The reaction mixture was cooled to room temperature, the blue crystals filtered off, washed with distilled water (100 mL) and finally air dried; yield 3.9 g (73%), melting point $> 280^\circ\text{C}$, IR (KBr, cm^{-1}) : 3420 (ms,br) ($\nu(\text{O-H})$); 3074 (ms) and 3026 (ms) ($\nu(\text{C-H})$); 1680 (s) and 1640 (ms) ($\nu_{\text{asym}}(\text{C=O})$).

- Cu(dipic)(py)⁵⁰

Pyridine-2,6-dicarboxylatocopper (II) dihydrate (0.4g, 1.5 mmol) was added to 125 mL of reagent grade pyridine. The mixture was boiled and stirred until the dark blue solution had a volume of 30 mL and precipitation had started at this point. After cooling the solution to room temperature, the azure blue product was filtered and air dried overnight : yield 0.3 g (58%), melting point > 280⁰C, IR (KBr, cm⁻¹) : 3090 (ms) and 3063 (ms) (ν(C-H)); 1675 (s) and 1637 (s) (ν_{asym}(C=O)).

- Cu salen⁵¹

Bis (salicylaldehyde) *N,N'*-ethylenediimine (2.7 g, 0.01 mol) was dissolved in *N,N'*-dimethylformamide (DMF) 30 mL at 60⁰C. After stirring the solution until homogeneity, cupric acetate monohydrate (2.0 g, 0.01 mol) dissolved in DMF was dropped slowly and precipitation of Cu salen had occurred. The green product was filtered and washed with acetone : yield 3.0 g (91%), melting point > 280⁰C, IR (KBr, cm⁻¹) : 3500 (ws,br) (ν(O-H)); 3020 (ws) (ν(C-H)), 2950 (ws) (ν(C-H)), 1640 (s) (ν(C=N)).

- Cyclohexyl azide⁵²

Cyclohexyl bromide (0.08 mol) was added to a stirred 25% aqueous solution of sodium azide (10.2 g, 0.16 mol). Aliquot[®] (1.6 g, 0.004 mol) was added and the mixture heated to 100⁰C with vigorous stirring. When all the starting material was consumed, the mixture was cooled and the phases were separated. The organic layer was dried with a small amount of magnesium sulfate, the solvent evaporated, and the product distilled at reduced pressure; yield 7.5 g (74%), boiling point 74⁰C, IR (neat, cm⁻¹) : 2940 (s) and 2853 (s) (ν(C-H)), 2095 (s) (ν(C-N)).

General Procedure for the Oxidation of Cyclohexane

A typical oxidation reaction was performed in a solution of pyridine (30 mL), cyclohexane (20 mmol), cupric acetate monohydrate or other appropriate copper catalysts (0.2 mmol) and acetic acid (3.0 mL). After adding 30% H₂O₂ (15 mmol) to

commence the oxidation reaction, the reaction mixture was stirred for 16 h at room temperature.

General Work-up Procedure

An aliquot of the reaction mixture 1.0 mL was acidified with cold 25% H₂SO₄. The mixture was then extracted with diethyl ether (2 x 2 mL). The ethereal extract was separated and successively washed with saturated sodium hydrogen carbonate 2.0 mL. Finally, the ethereal extract was dried over anhydrous sodium sulfate. The resulting solution was analyzed by Gas Chromatography after the addition of the exact amount of an appropriate internal standard.

Competitive Studies on the Relative Reactivity of Cyclic Saturated Hydrocarbons

According to the general oxidation procedure, equimolar amount (10 mmol each) of cyclohexane and either cyclopentane, cycloheptane, cyclooctane or cyclododecane, respectively, were used as substrates in the reaction.

Competitive Studies on the Oxidation of Cyclohexane, Cyclohexene, and Ethylbenzene

According to the general oxidation procedure, equimolar amount (10 mmol each) of cyclohexane and either cyclohexene or ethylbenzene were used as substrates in the oxidation reaction.

Chemoselectivity Studies

Following the general oxidation procedure, cyclohexanol, ethanol, isopropanol, ethylene glycol, biphenyl, anisole, methyl benzoate, diphenyl sulfide, and triphenylphosphine, respectively, were added as a co-substrate to the oxidation reaction of cyclooctane.

Effect of Oxidizing Agent : Hydrogen Peroxide, Urea.hydrogen Peroxide and *tert*-Butyl Hydroperoxide (TBHP)

The oxidation reaction was carried out in the same manner as previously described, but urea.hydrogen peroxide and *tert*-butyl hydroperoxide were used to replace hydrogen peroxide.

General Procedure for the Construction of C-Cl, C-Br and C-N Bonds

The oxidation reaction of hydrocarbon (50 mmol) was carried out in the presence of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.5 mmol), LiCl or BrCCl_3 or NaN_3 in pyridine (30 mL) and acetic acid (1.0 mL). The temperature of the reaction was raised up to $55\text{-}60^\circ\text{C}$ and TBHP (10 mmol) was added. The kinetic analysis or the quantification followed the general procedure described earlier.