

CHAPTER II

EXPERIMENTAL SECTION

2.1 General procedure

Thin layer chromatography (TLC) was carried out on aluminium sheet precoated with silica gel (Merck's, Kieselgel 60 PF₂₅₄). Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G Art 7734 (70-230 mesh)). Melting points were determined with a John – Fisher melting point apparatus and are uncorrected.

2.2 Instrumentation

The FTIR spectra were recorded on a Fourier Transform Infrared spectrophotometer Nicolet model Impact 410, solid samples were incorporated to potassium bromide to form a pellet. The ¹H-NMR spectra were obtained in deuterated chloroform (CDCl₃) with tetramethylsilane (TMS) as an internal reference on a Bruker model ACF 200 spectrometer. Gas chromatographic analysis was carried out on a Shimadzu gas chromatograph 9A instrument equipped with flame ionization detector with N₂ as a carrier gas. The column used for chromatography was a capillary column type of DB-wax (30 m x 0.250 mm) from J&W Scientific company.

2.3 Chemicals

All solvents used in this research were purified before use by standard methodology except for reagent grade solvents. The reagents for synthesizing metal stearate complexes and all organic substrates, *e.g.* cyclohexane, *tert*-butylcyclohexane, methylcyclohexane *etc.*, were purchased from Fluka chemical company and were used without further purification.

2.4 Syntheses

2.4.1 Metal stearate complexes

General procedure for the syntheses of metal stearate complexes

Stearic acid (6.26 g, 22 mmol) was dissolved in 1 M sodium hydroxide solution at 80°C. After solution was stirred until homogeneity, selected transition metal salt (7.3 mmol) dissolved in water (10 mL) was added dropwise. The mixture was allowed to stir for another 3 min, then the precipitation was collected and dried *in vacuo* [19].

Cr(III)stearate : blue gray solid (85%), m.p. 100-103°C. IR (KBr, cm⁻¹): 2846-2903 (w), 1536-1705 (b), 1461 (s), 723 (s)

Co(II)stearate : pink solid (74%), m.p. 86-90°C. IR (KBr, cm⁻¹): 2848-2913 (w), 1630-1701 (b), 1556 (s)

Ni(II)stearate : light green solid (87 %), m.p. 175-177°C. IR (KBr, cm⁻¹): 2856-2912 (w), 1564-1720 (w), 1381 (b), 721 (s)

Mn(II)stearate : white solid (85%), m.p. 108-111°C. IR (KBr, cm⁻¹): 2856 (b), 1569-1720 (s), 1461 (s), 718 (s)

Fe(III)stearate : orange solid (78%), m.p. 94-96°C. IR (KBr, cm⁻¹): 2846-2912 (w), 1705 (s), 1583 (s), 1461 (s), 723 (s)

Cu(II)stearate : light blue solid (90%), m.p. 138-145°C. IR (KBr, cm⁻¹): 2903 (s), 2846 (s), 1592 (s), 1404-1456 (w), 721 (s)

2.4.2 Syntheses of authentic compounds

2.4.2.1 Syntheses of 3- *tert*-butylcyclohexanone

tert-Butylchloride 0.920 g (10 mmol) was added to magnesium turnings 0.394 g (16.40 mmol) in 30 mL of anhydrous ether. The reaction was started by the addition of a catalytic amount of iodine. The remaining *tert*-butylchloride in 40 mL of ether was added with stirring for 30 min. The mixture was then refluxed for 30 min and cooled in ice. 2-Cyclohexen-1-one 0.430 g (5 mmol) in 10 mL of ether was added dropwise, followed by stirring at RT for 4 hr and refluxing for 1 hr.

The solution was cooled and poured into 4 mL of ice cold 1 M HCl. The phases were separated and the aqueous phase was extracted twice with 10 mL

of ether. The combined ether layers were washed with saturated NaHCO_3 and NaCl solutions, dried over anhydrous Na_2SO_4 and the rest solvent was evaporated [20].

3-*tert*-butylcyclohexanone: Liquid, colorless. $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 0.90 (12H, s), 1.84-1.87 (5H, m), 3.73-3.76 (4H, m); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 207.1 (1C : C=O), 77.4 (1C), 77.1 (1C), 76.8 (1C), 30.6 (1C), 30.9 (3C), 27.2 (1C) and 25.6 (1C).

2.4.2.2 Syntheses of 2-, 3- and 4- *tert*-butylcyclohexanol

General procedure [21]: Sodium borohydride 0.380 g (10 mmol) was added over a period of 5 min to a stirred solution of 20 mmol of interested ketone in 10 mL of ethanol. The reaction mixture was stirred for 2 h at room temperature, then 10 mL of water was added. The mixture was extracted three times with 10 mL of ether. The combined organic phases were washed with saturated NaCl solution and dried over Na_2SO_4 . The solvent was evaporated and the residue was collected in vacuum desiccator.

2-*tert*-butylcyclohexanol: Liquid, colorless, IR (KBr, cm^{-1}): 3409, 2931, 1475, 1061 and 967; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.14-1.18 (9H, m), 1.45-1.49 (9H, m), 3.46 (1H, s) and 4.22 (1H, s).

3- *tert*-butylcyclohexanol: Liquid, colorless, IR (KBr, cm^{-1}): 3294, 2936, 2869, 1467, 1365 and 1070; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 0.77-1.16 (9H, m), 1.67-1.98 (9H, m), 3.46 (1H, s) and 4.38 (1H, s).

4- *tert*-butylcyclohexanol: White solid, mp 60°C , IR (KBr, cm^{-1}): 3288, 2941, 2856, 1452, 1376 and 1066; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 0.83-1.21 (9H, m), 1.74-2.00 (9H, m), 3.49 (1H, m) and 4.00 (1H, m).

2.4.2.3 Syntheses of 2- and 3- hexanol

2- and 3- Hexanols were prepared using the same reaction conditions as described in the general procedure in 2.4.2.2, but the ketone was changed to 2- and 3-hexanones.

2-Hexanol: Liquid, colorless, IR (KBr, cm^{-1}): 3405, 2955, 2863, 1634, 1116, 1055; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 0.92-0.96 (3H, t, $J = 6.92$ Hz), 1.21-1.22 (3H, d, $J = 6.18$), 1.34-1.50 (6H, m), 2.2 (1H, s) and 3.80-3.85 (1H, s); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 68.2 (1C, C-O), 39.1 (1C), 28.0 (1C), 23.5 (1C), 22.7 (1C) and 14.1 (1C).

3-Hexanol: Liquid, colorless, IR (KBr, cm^{-1}): 3396, 2955, 2871, 1639, 1465; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 0.91-0.96 (6H, m), 1.32-1.55 (6H, m), 2.0 (1H, s) and 3.54-3.57 (1H, m); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm) : 73.0 (1C, C-O), 39.1 (1C), 30.1 (1C), 18.8 (1C), 14.1 (1C) and 9.9 (1C).

2.4.2.4 Syntheses of cyclohexyl acetate

Cyclohexanol 5.008 g (50 mmol), 12 mL of acetic anhydride and 0.4 mL of anhydrous pyridine were refluxed for 1.5 h. The cooled solution was poured into 15 mL of 2% HCl at 0 °C and the mixture was extracted three times with 15 mL of 2% NaOH, dried over Na_2SO_4 and evaporated *in vacuo* [21].

Cyclohexyl acetate: Liquid, colorless, IR (KBr, cm^{-1}): 2932, 2854, 1728, 1445, 1363, 1238; $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.25-1.34 (6H, m), 1.39-1.44 (4H, m), 2.06 (3H, s) and 3.68-3.62 (1H, m); $^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 168.2 (1C : C=O), 73.4 (1C : C-O), 33.1 (2C), 27.4 (1C), 24.0 (2C) and 22.3 (1C).

2.5 The general procedure for the oxidation of hydrocarbons

Metal stearate (0.2 mmol) was added to hydrocarbon substrate (50 mmol) in a round bottom flask, 70% TBHP (9.0 mmol) was added. 5 mL of isooctane was used as a solvent when the total volume of the reaction was smaller than 4 mL or a substrate was solid. The mixture was stirred at 70°C for 24 hr. After the reaction was finished, 1 mL of the reaction mixture was taken and extracted with diethyl ether. The combined extracts were washed with 25% H_2SO_4 and saturated solution of NaHCO_3 , respectively. The organic layer was dried over anhydrous Na_2SO_4 and analyzed by gas chromatograph (GC) with the addition of an exact amount of appropriate internal standard.

2.6 Chemoselectivity study on cyclohexane oxidation

2.6.1 Effect of metal stearate complexes

The oxidation of cyclohexane was conducted as described in general procedure by employing six metal stearate complexes: Cr(III), Co(II), Ni(II), Mn(II), Fe(III) and Cu(II) stearates.

2.6.2 Effect of bi- and tri- catalysts

Effect of the ratio of bicatalysts

The cyclohexane oxidation reaction was conducted as described in general procedure using Cr(III) and Co(II) stearates with a ratio of 1:1, 2:1, 3:1 and 4:1.

Effect of type of bicatalysts

The oxidation reaction was carried out as described in general procedure but using bicatalysts of other metal stearates such as Co(II), Cu(II), Ni(II), Mn(II) and Fe(III) stearates together with Cr(III) stearate as a main catalyst in 3:1 ratio.

Effect of tricatalysts

The oxidation reaction was carried out as stated in general procedure using Cr(III) stearate and two types of other metal stearates as a tricatalysts. The ratio of Cr(III) stearate and two types of metal stearates was Cr:M1:M2 as 2:1:1.

2.7 Kinetic study on the reaction rate of cyclohexane oxidation

The general oxidation procedure of cyclohexane using Cr(III) stearate, Co(II) stearate and bicatalyst (Cr(III) : Co(II) stearates as 3 : 1) as catalysts was carried out. At different reaction time proceeded (1, 2, 3, 5 and 8 hr), an aliquot from the reaction mixture was taken, worked up and analyzed by GC.

2.8 The effect of the amount of Co(II) stearate on the oxidation of cyclohexane

The oxidation reaction was conducted as aforementioned in general procedure using Co(II) stearate as catalyst, but different amount of Co(II) stearate was varied (0.1, 0.2, 0.3 and 0.5 mmol).

2.9 The oxidation reaction of other selected organic substrates

The oxidation reaction was carried out as described in the general procedure by using Cr(III) stearate as a catalyst and different types of substrate including cyclohexyl acetate, cyclohexanol and cyclohexanone were examined.

2.10 Effect of additives

The oxidation of cyclohexane was carried out as described in the general procedure. Carbon tetrachloride and bromotrichloromethane were separately added to the oxidation reaction to observe the effect of additive.

2.11 Regioselectivity study

Cr(III) stearate was employed as catalyst in *tert*-butylcyclohexane, *n*-hexane, adamantane and methylcyclohexane oxidation using reaction conditions described in the general procedure.

2.12 The effect of the amount of TBHP on Cr(III)stearate oxidation of *n*-hexane

The oxidation reaction was carried out as presented in the general procedure by using Cr(III) stearate as catalyst, but the amount of TBHP was varied (3, 9 and 18 mmol).

2.13 The study on adamantane oxidation catalyzed by bicatalysts of metal stearate complexes

The oxidation of admantane was carried out as described in the general procedure using bicatalysts of other metal stearates such as Co(II), Cu(II), Ni(II), Mn(II) and Fe(III) stearates together with Cr(III) stearate as a main catalyst in a ratio of 3:1.

2.14 The oxidation of cyclohexane catalyzed by Cr(III) stearate in the large scale

The oxidation of cyclohexane in large scale (500 mmol) was carried out as mentioned in the general procedure using Cr(III) stearate as catalyst.

2.15 The kinetic study on cyclohexane oxidation catalyzed by Cr(III) stearate in the presence of triphenylphosphine

Following the general procedure of the oxidation reaction, at different reaction time proceeded (1, 3, 5 and 8 hr), 1 mL of reaction mixture was added a little amount of PPh₃ (approximately 0.2 g) before working up, then worked up following the general procedure and analyzed by GC.