CHAPTER II

EXPERIMENTAL SECTION

2.1 General procedure

Characterization of unknown samples could be conducted by different spectroscopic techniques. Melting points (m.p.) were determined with a Fisher-Johns melting point apparatus and are uncorrected. The FT-IR spectra were performed on a Fourier Transform Infrared Spectrophotometer on Nicolet model Impact 410. Solid samples were incorporated to potassium bromide (KBr) to form pellet. The ¹H and ¹³C-NMR spectra were obtained in deuterated chloroform (CDCl₃) or otherwised stated, with Bruker model ACF200 and Varian model Mercury 400 spectrometers.

Chromatography test: thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF₂₅₄). Column chromatography was performed on silica gel (Merck's, Kieselgel 60G). Gas chromatography analysis was carried out on a Shimadzu GC-14A Gas Chromatograph equipped with flame ionization detector (FID) using 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.

2.2 Chemicals

All solvents used for this research were purified prior to use by standard methodology except for those which were reagent grade; for example, carbon tetrachloride, chloroform and *N*,*N*-dimethylformamide (DMF). The reagents used for synthesizing metal carboxylate complexs, substrates for oxidation and all carbonyl compounds were purchased from Fluka chemical company and were used without further purification. Merck's silica gel 60 G Art 7734 (70-230 mesh) was used as adsorbent for column.

2.3 Syntheses

2.3.1 Metal stearate complexes.

- Cr(III) stearate

Stearic acid (22 mmol) was dissolved in 1 M sodium hydroxide solution at 80°C. After the mixture was heated and transmuted homogeneously, a solution of chromium(III) chloride hexahydrate (7 mmol) dissolved in water 10 mL was added dropwise. The mixture was continued heating at about 80 °C for about 30 min, the precipitate was collected and dried in vacuo. The Cr(III) stearate 86% yield as a blue grey solid was obtained.

Cr(III) stearate: blue gray solid (86 %), m.p. 100-103 °C. IR (KBr, cm⁻¹): 2856-2921 (w), 1720 (s), 1569 (s), 1461 (s) and 723 (s).

General procedure for the syntheses of metal stearate complexes

The preparation of various metal stearates could be accomplished by employing the general procedure as aforementioned.

Co(II) stearate: pink solid (74%), m.p. 86-90 ^OC. IR (KBr, cm⁻¹): 2856-2912 (w), 1630-1701 (b), 1545 (s), 2856-2912 (w), 1630-1701 (b), 1545 (s) and 721 (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) and 723 (s).

Ni(II) stearate: light green solid (87%), m.p. 175-177 °C. IR (KBr, cm⁻¹): 2856-2903 (w), 1564-1720 (w), 1381 (b) and 721 (s).

Mn(II) stearate: white solid (90%), m.p. 108-111 °C. IR (KBr, cm⁻¹): 2856 (b), 1569-1720 (w), 1461 (s) and 718 (s).

Cu(II) stearate: light blue solid (92%), m.p. 138-145 °C. IR (KBr, cm⁻¹): 2903 (s), 2846 (s), 1592 (s), 1404-1456 (w) and 721 (s).

2.3.2 Chromium(III) carboxylate complexes.

The preparation of various chromium(III) carboxylate complexes was carried out using previous described procedure.

Cr(III) palmitate: blue gray solid (81%), m.p. 115-120 °C. IR (KBr, cm⁻¹): 2912 (s), 2846 (s), 1705 (s), 1532 (s), 1461 (s) and 721 (s).

Cr(III) behenate: blue gray solid (84%), m.p. 125-130 °C. IR (KBr, cm⁻¹): 2856-2912 (w), 1705 (s), 1541(s), 1461 (s) and 721 (s).

Cr(III) naphthenate: green gray solid (83%), m.p.99-101 °C. IR (KBr, cm⁻¹): 3043 (s), 2837-2921 (w), 1767 (w), 1409 (s) and 787 (s)

Cr(III) acetylacetonate [Cr(acac)₃]¹⁹

Chromium(III) chloride hexahydrate (2.66 g; 10 mmol) was dissolved in distilled water 3 mL and the mixture was heated until homogeneity. After that concentrated ammonium hydroxide 4.5 mL was dropped slowly. The solution was stirred about 15-20 min on water bath (~ 80° C) and brown precipitate occurred. The brown solid was filtered off and washed with distilled water until no more chloride detected. Place the precipitate in Erlenmeyer flask, acetylacetone (6 mL; 10 mmol) was slowly dropped for 35 min on water bath (~ 80° C) and the precipitation of red solid occurred. The products were filtered and recrystallized by 95% ethanol. The blue gray solid of Cr(acac)₃ was obtained (75 %), m.p. 209-215 °C. IR (KBr, cm⁻¹): 1564-1640 (w), 1381 (s), 1282 (s), 1028 (s) and 512 (s).

2.4 Study on the optimum conditions for the oxidation of benzylic

methylene compounds.

2.4.1 General procedure

To a solution of substrate (5 mmol) in isooctane (5 mL) containing Cr(III) stearate 0.2 mmol in a round bottom flask, 70% TBHP (9 mmol) was added. The mixture was stirred at 70°C for 24 hours. After the reaction 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 sodium hydrogen carbonate (NaHCO₃), respectively. The organic layer was dried over anhydrous Na₂SO₄ and analyzed by gas chromatography (GC) with the addition of an exact amount of appropriate internal standard.

2.4.2 Effect of metal stearate

The oxidation reaction was carried out in the same manner as previously described employing five metal stearate complexes: Fe(III), Mn(II), Co(II), Cu(II) and Ni(II) stearates.

2.4.3 Effect of chromium carboxylate

The oxidation reaction was carried out in the same manner as the former, switching from Cr(III) stearate complex to : Cr(III) palmitate, Cr(III) behenate, Cr(III) naphthenate and Cr(III) acetylacetonate The total yield of product (alcohol and ketone) and selectivity of the reaction were determined.

2.4.4 Effect of the amount of catalyst

The oxidation reaction was carried out in the same manner as aforementioned, but the amount of catalyst was varied : 0.05, 0.10, 0.15, 0.20, 0.25 mmol.

2.4.5 Effect of solvents

The oxidation reaction was carried out in the same manner as described above except for the DMF, tetrahydrofuran (THF), dichloromethane, 1,2-dichloroethane, ethanol, methanol, carbon tetrachloride (CCl₄), acetone, chloroform, pyridine and acetonitrile was used as a reaction medium.

2.4.6 Effect of the amount of solvent

The oxidation reaction was carried out in the same manner as previously described, but the amount of the solvent was varied : 5, 10, 15 mL

2.4.7 Effect of type of oxidants

The oxidation reaction was carried out in the same manner as aforementioned, switching from TBHP to zinc grit and AcOH, 2-ethylbutylraldehyde and O_2 .

2.4.8 Effect of the amount of oxidants

The oxidation reaction was carried out the same as previously studied, but the amount of oxidant was varied: 0, 3, 6, 9 and 12 mmol.

2.5 Comparative kinetic study on the oxidation of ethylbenzene catalyzed

by Cr(III) stearate

The selective benzylic oxidation catalyzed by chromium(III) stearate as a catalyst was carried out at 70 °C. At different reaction times proceeded: 0.5, 1, 1.5, 2, 3, 4, 5, 8, 11, 14, 19, 21 and 24 hr, the sample (1 mL) of the reaction mixture was taken, worked up with 25% H₂SO₄, saturated NaHCO₃ and dried over anhydrous Na₂SO₄ as previously described, analyzed by GC or ¹H-NMR spectrometer.

2.6 Oxidation of various benzylic methylene compounds.

Selected benzylic methylene compounds, namely, toluene, ethylbenzene, propylbenzene, butylbenzene, *sec*-butylbenzene, *tert*-butylbenzene, pentylbenzene, 1,2,3,4-tetrahydronaphthalene, 1,2,3,4-tetrahydroquinoline, xanthene, benzyl alcohol, benzaldehyde, acenaphthene, α -tetralone, dibenzyl ether, benzyl ethyl ether, benzyl hexyl ether, benzyl acetate, ethyl benzoate, ethyl 4-ethylbenzoate, ethyl phenylacetate, 1bromo-2-ethylbenzene, 1-ethyl-2-nitrobenzene and 4-ethylbenzoic acid were oxidized according to the procedure previously described. The aliquot (1 mL) of the reaction mixture was taken, worked up with 25% H₂SO₄, saturated NaHCO₃ and dried over anhydrous Na₂SO₄, analyzed by GC or ¹H-NMR spectrometer.

General isolation procedure.

After the reaction was complete (followed by TLC), the oxidation product was separated as follows: The whole reaction mixture was extracted according to the general procedure and all the solvents were removed. The crude product was purified by silica gel column chromatography using a mixture of hexane - ethyl acetate or chloroform – ethyl acetate as an eluent. The equivalent fractions monitered by TLC were combined and

the solvents were completely evaporated. The residue was recrystallized by an appropriate solvent or chromatographed over silica gel column to yield the desired carbonyl compound.

Benzoic acid: 91% yield (from the oxidation of benzyl alcohol), 85% yield (from the oxidation of benzaldehyde) and 12% yield (from the oxidation of toluene) m.p. 122-124°C (H₂O), R_f 0.79 (hexane-ethyl acetate (7:1)) IR (KBr) 3000, 1715 and 925 cm⁻¹, ¹H-NMR (CDCl₃) δ (ppm): 7.29 (t, J = 6.00 Hz, 1H), 7.46 (t, J = 7.11 Hz, 1H), 7.58 (t, J = 6.10 Hz, 1H) and 8.10 (d, J = 7.05 Hz, 2H).

Propiophenone : 92% yield b.p. 87-90°C, R_f 0.52 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 1.21 (t, J = 6.37 Hz, 3H), 3.00 (q, J = 5.06 Hz , 2H), 7.37-7.52 (m, 3H) and 7.94 (dd, J = 6.73, 1.65 Hz , 2H)

Butyrophenone : 76% yield b.p. 99 – 101°C, R_f 0.33 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 0.97 (t, J = 6.30 Hz, 3H), 1.41-1.74 (m, 2H), 2.93 (t, J = 7.17 Hz, 2H), 7.43-7.50 (m, 3H) and 7.95 (dd, J = 8.14, 1.12 Hz, 2H)

Valerophenone : 80% yield b.p. 243 – 245°C, R_f 0.54 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 0.93 (t, J = 6.96 Hz, 3H), 1.30-1.45 (m, 2H), 1.74 (qin, J = 6.96 Hz, 2H), 2.91 (t, J = 5.50 Hz, 2H), 7.25 (t, J = 2.24 Hz, 1H), 7.46 (dt, J = 11.80, 1.65 Hz, 2H) and 7.94 (d, J = 4.99 Hz, 2H)

3-Phenylbutan-2-one : 40% yield b.p. 93-95 °C R_f 0.56 (hexane-ethyl acetate (7:1)) IR (KBr) 2840-3000, 1700, 1438, 1295 and 900-950 cm^{-1 ·1}H-NMR (CDCl₃) δ (ppm): 1.46 (d, J = 6.34 Hz, 3H), 1.87 (q, J = 7.20 Hz,1H), 2.20 (s, 3H), 7.29 (t, J = 4.40 Hz, 1H), 7.37 (t, J = 7.20 Hz, 1H), 7.50 (t, J = 7.60 Hz, 1H), 7.60 (d, J = 7.60 Hz, 1H) and 8.0 (d, J = 6.80 Hz, 1H)

 α -Tetralone : 40% yield b.p 125-127 °C, R_f 0.54 (hexane-ethyl acetate (7:1)) 2.12 (qin, J = 6.15 Hz , 2H) 2.64 (t, J = 6.13 Hz, 4H) 7.24 (t, J = 7.45 Hz, 1H) 7.32 (d, J = 8.13 Hz , 1H) 7.45 (t, J = 7.41 Hz , 1H) and 8.01 (d, J = 7.62 Hz, 1H)

1-(3, 4-Dihydro-2H-quinolin-1-yl)-2, 2-dimethyl-propan-1-one: 83% yield. IR(KBr): 2962, 1631, 1600, 1489, 1405, 1363, 1152 and 950 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 1.32 (s, 9H), 2.02 (qin, J = 6.40 Hz, 2H), 2.79 (t, J = 7.20 Hz, 2H), 3.81(t, J = 6.00 Hz, 2H), 7.13-7.17 (m, 2H), 7.30 (d, J = 8.00 Hz, 1H) and 7.40 (d, J = 8.00 Hz, 1H) *1-(2,2-Dimethyl-propionyl)-2,3-dihydro-1H-quinolin-4-one:* 91% yield IR(KBr) : 3062, 2900-2960, 1687, 1640, 1475, 1362, 1152, 1117, 970, 900 and 777 cm^{-1 1}H-NMR (CDCl₃) δ (ppm): 1.28 (s, 9H), 1.98 (qin, *J* = 6.80 Hz, 2H), 2.75 (t, *J* = 7.20 Hz, 2H), 3.77 (t, *J* = 5.20 Hz, 2H), 7.07-7.26 (m, 3H) and 7.35 (t, *J* = 8.00 Hz, 1H)

2,3-Dihydro-1H-quinolin-4-one: 74% yield m.p.78-80 °C, $R_f 0.10$ (hexane-ethyl acetate (7:1) IR (KBr) :3460, 2910, 2850, 2360, 1705, 1643 and 1163 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 2.78 (t, J = 6.80 Hz, 2H), 4.22 (J = 6.00 Hz, 2H), 7.21 (t, J = 7.20 Hz, 1H), 7.49 (t, J = 7.20 Hz, 1H), 7.62 (d, J = 8.80 Hz, 1H) and 7.99 (d, J = 7.20 Hz, 1H)

Xanthone : 93% yield m.p. 171-174 °C, R_f 0.54 (hexane-ethyl acetate (7:1)) IR (KBr) : 3053, 1602-1658, 1263 and 930 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 7.35 (d, J = 7.79 Hz , 2H), 7.47 (t, J = 8.57 Hz, 2H), 7.72 (t, J = 8.74 Hz , 2H) 8.34 (d, J = 7.89 Hz, 2H)

Acenaphthenequinone: 90% yield. m.p. 257-260 °C, R_f 0.69 (hexane-ethyl acetate (7:1) IR (KBr) : 3033, 2918, 1710, 1225-1270 and 820 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 7.52 (dt, J = 30.00, 8.34 Hz, 2H), 7.77 (dd, J = 10.34, 8.88 Hz, 2H) and 8.02 (dd, J = 17.25, 8.88 Hz, 2H)

2,3-Dihydro-1,4-naphthoquinone : 99% yield m.p. 120–124°C R_f 0.30 (hexaneethyl acetate (7:1)) IR (KBr) : 3436, 2922, 2853, 1670, 1585, 1408, 1256 and 680-770 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 2.16 (s, 4H) and 7.52 (t, J = 8.10 Hz , 2H) and 8.08 (d, J = 6.92 Hz, 2H)

Benzyl ethyl ether: 83% yield b.p.62 °C, R_f 0.50 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 1.27 (t, J = 5.66 Hz, 3H), 3.53 (q, J = 7.05 Hz, 2H), 4.54 (s, 2H) and 7.24-7.37(m, 4H)

Benzyl hexyl ether: 81% yield R_f 0.54 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 0.92 (t, J = 7.20 Hz, 3H), 1.35-1.69 (m, 8H), 3.51 (t, J = 9.20 Hz, 2H), 4.54 (s, 2H) and 7.30-7.44 (m, 5H)

Acetyl benzoate: 74% yield m.p. 55-56 °C (from oxidation of benzyl ethyl ether), 68% yield (from oxidation of benzyl acetate) and 13% yield from oxidation of ethyl benzoate) Rf 0.31(chloroform-ethyl acetate (9:1)) IR (KBr) : 3456, 2850-2920, 1700 and 1300 cm^{-1 1}H-NMR (CDCl₃) δ (ppm): 1.29 (s, 3H), 7.46 (t, J = 7.71 Hz, 2H), 7.61 (t, J =7.50 Hz, 1H) and 8.10 (d, J = 7.28 Hz, 2H) *Hexanoyl benzoate*: 72% yield m.p. 59-60 °C R_f 0.37 (hexane-ethyl acetate (7:1)) IR (KBr) : 3440, 2931, 2358, 1760 and 1242 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 1.00 (t, J = 6.8 Hz, 3H), 1.29 (qin, J = 13.60 Hz, 2H), 1.34-1.38 (m, 2H), 1.57 (qin, J = 14.40 Hz, 2H), 2.16 (t, J = 1.20 Hz, 2H), 7.46 (t, J = 6.40 Hz, 2H), 7.59 (t, J = 8.00 Hz, 1H) and 7.95 (d, J = 8.40 Hz, 2H)

Benzoic anhydride : 81% yield m.p. 39-43°C R_f 0.19(hexane-ethyl acetate (7:1)) IR (KBr) : 3071, 2800-2980, 1690, 1040 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 7.47 (t, J = 7.05 Hz, 4H), 7.61 (t, J = 7.33 Hz, 2H) and 8.10 (d, J = 7.11 Hz, 4H)

Benzyl acetate: 85% yield b.p. 215-217°C R_f 0.61 (hexane-ethyl acetate (7:1)) Rf 0.75 (chloroform-ethyl acetate (9:1)) ¹H-NMR (CDCl₃) δ (ppm): 2.09 (s, 3H), 5.09 (s, 2H), and 7.24-7.40 (m, 5H)

Ethyl benzoate: 80.24% yield b.p. 210-213°C R_f 0.56 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 1.38 (t, J = 7.10 Hz, 3H), 4.36 (q, 7.14 Hz, 2H) 7.51 (t, J = 3.19 Hz, 2H) 7.57 (t, J = 1.54 Hz, 1H) and 8.03 (dd, J = 3.20, 1.61 Hz, 2H)

Ethyl 4-ethylbenzoate : 88% yield R_f 0.51(hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 1.16 (t, J = 7.60 Hz, 3H), 1.29 (t, J = 7.22 Hz, 3H), 4.27(q, J = 7.12 Hz, 4H), 7.15(d, J = 4.71 Hz, 2H) and 7.86 (d, J = 8.03 Hz, 2H)

Ethyl phenylacetate : 88% yield. b.p. 226 °C R_f 0.43 (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 1.31 (t, *J* = 8.00 Hz, 3H), 3.67 (2H, s), 4.21 (q, *J* = 7.20 Hz, 2H), 7.30-7.40 (m, 5H)

4-Acetylbenzoylacetate : 87% yield m.p. 54-56 °C R_f 0.23 (hexane-ethyl acetate (7:1)) IR (KBr) : 2850-2990, 1680-1710, 1282, 1105-1135 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 1.41 (t, J = 6.80 Hz, 3H), 2.64 (s, 3H), 4.40 (q, J = 6.80 Hz, 2H), 7.80 (d, J = 6.80 Hz, 2H) and 8.12 (d, J = 8.00 Hz, 2H)

Oxophenylacetic acid ethylester : 87% yield (from oxidation of ethyl phenylacetate with TBHP 9 mmol), 89% yield (from oxidation of ethyl phenylacetate with TBHP 18 mmol) m.p. 61-63 °C, R_f 0.34 (hexane-ethyl acetate (7:1)) IR (KBr) : 2912, 2853, 1703, 1430-1465, 1300, 933 and 719 cm^{-1 1}H-NMR (CDCl₃) δ (ppm): 1.46 (t, J = 7.20 Hz, 3H), 4.49 (q, J = 6.40 Hz, 2H), 7.55 (t, J = 8.00 Hz, 2H), 7.70 (t, J = 8.00 Hz, 1H) and 8.05 (d, J = 6.80 Hz, 2H)

2-Bromoacetophenone : 57% yield $R_f 0.29$ (hexane-ethyl acetate (7:1)) ¹H-NMR (CDCl₃) δ (ppm): 1.41(s, 3H), 7.04 (dd, J = 8.06, 4.11 Hz, 2H), 7.22 (d, J = 4.02 Hz, 1H) and 7.51(d, J = 7.74 Hz, 1H)

2-Nitroacetophenone : 53% yield m.p. 23-25°C R_f 0.14 (hexane-ethyl acetate (7:1)) and 0.38 (chloroform-ethyl acetate (9:1)) IR (KBr) : 2840-2920, 2360, 1701, 1532, 1358 and 1080-1110 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 2.55(s, 3H), 7.63 (t, J = 8.80 Hz, 1H), 7.70 (t, J = 7.60 Hz, 1H), 7.84 (d, J = 7.60 Hz, 1H) and 7.89 (d, J = 8.00 Hz, 1H)

4-Acetylbenzoic acid : 53% yield m.p. 208-210°C R_f 0.19 (chloroform-ethyl acetate (9:1)) IR (KBr): 2570-3335, 1687, 1564, 1423, 1260-1292, 932, 864 and 770 cm⁻¹ ¹H-NMR (CDCl₃) δ (ppm): 2.65 (s, 3H), 8.02 (d, J = 6.60 Hz ,2H) and 8.18 (d, J = 7.91 Hz, 2H)

2.7 Competitive studies of the oxidation of ethylbenzene, 1-bromo-2ethylbenzene, 1-ethyl-2-nitrobenzene and ethyl 4-ethylbenzoate

Following the general oxidation procedure, equimolar amount (5 mmol) of ethylbenzene and 1-bromo-2-ethylbenzene; and 1-ethyl-2-nitrobenzene and ethyl 4ethylbenzoate were used as competitive substrates in the reaction. Competition reaction between the oxidation of ethylbenzene and 1-bromo-2-ethylbenzene or that between the oxidation of ethylbenzene and 1-ethyl-2-nitrobenzene or that between ethylbenzene and ethyl 4-ethylbenzoate were carried out.

2.8 Oxidation of ethylbenzene catalyzed by bicatalyst and tricatalyst

The oxidation reactions of ethylbenzene catalyzed by bicatalysts and tricatalysts were conducted. These reactions were carried out at 70°C, at different ratio of catalyst: Cr(III) stearate and other metal stearates in ratio of 1:1, 2:1, 3:1 and 4:1. Furthermore, tricatalyst was used in these reactions in ratio of Cr(III) stearate and other metal stearates : 1:1:1 and 2:1:1. Other procedures were carried out as the same manner as mentioned above. Metal stearate tried in this examination included Fe(III), Mn(II), Co(II), Cu(II) and Ni(II) stearates.