

CHAPTER II

EXPERIMENTAL

2.1 General procedure:

This section provides general information of general and/or specific reaction conditions and spectral data for compounds along with a representative ^1H NMR and ^{13}C -NMR spectrum. The reactions were monitored by analytical thin-layer chromatography on aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF254). Visualization was effected by ultraviolet light (254 nm), followed by dipping the plate into the appropriate stain. All reactions were stirred with Teflon-coated magnetic stir bars in condenser fitted round bottom flask. Removal of solvents was normally accomplished using a *Buchi* rotary evaporator connected to a vacuum pump.

Chromatography: Gas chromatography analysis was carried out on Shimadzu Gas Chromatography 9A instrument equipped with flame ionization with N_2 as a carrier gas. The columns used for analyze were HP5 20M. Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G Art 7734 (70-230 mesh)).

^1H - and ^{13}C -NMR spectra were recorded at 400 MHz on a *Varian* spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance of CDCl_3 (7.24 ppm).

Infrared spectra were recorded on a *Shimadzu* Fourier transform infrared spectrometer with 2 cm resolution in a solution cell. Infrared frequencies are reported in reciprocal centimeters (cm^{-1}).

Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected.

Elemental analysis was carried out on CHNS/O ANALYSER (Perkin Elmer PE2400 Series II) at Scientific and Technological Research Equipment Center Chulalongkorn University. Gaseous products freed by pyrolysis in high-purity oxygen

and were chromatographically separated by frontal analysis with quantitatively detected by thermal conductivity detector.

X-ray diffractometer (XRD): The XRD pattern of chromium(III)stearate was taken by Rigaku, DMAX 2002 Ultima Plus X-ray powder diffractometer equipped with a monochromator and Cu-target x-ray tube (40 kv, 30 mA) and angle of 2θ range 1.2 – 40 degree at Chemistry department, Faculty of Science, Chulalongkorn University.

Chemicals: All solvents in this research were purified according to the procedures described in the standard methodology except for reagents and solvents that were reagent grade. The reagents for preparation of chromium (III) stearate and for synthesizing some substrates as well as commercial available substrates, *e.g.* cyclohexene, cyclohexanol, 1-hexanol, α -pinene, benzyl alcohol, cinnamyl alcohol, menthol, cholestanol etc., were purchased from Fluka chemical company and were used without further purification.

2.2 Syntheses

2.2.1 Preparation of chromium (III)stearate

Stearic acid (6.26 g; 22 mmol) was dissolved in the solution of sodium hydroxide (0.88 g NaOH in 20 mL carbondioxide free water) at 80 °C to give a 2 M solution. The solution was stirred until clear and homogeneity, chromium trichloride hexahydrate (7.3 mmol) dissolved in 10 mL of distilled water was added giving a light purple precipitate. The reaction mixture was allowed to stir at the same temperature until complex occurred, then the precipitate was collected and dried *in vacuo* (75%), m.p. 100-103°C. IR (KBr, cm^{-1}): 2850-2900 (w), 1600-1700 (s), 1400-1450 (s).

2.2.2 Preparation of styrene diol (1-phenylethane-1,2-diol)

Into a rounded-bottom flask was placed styrene oxide 20 mmol (2.403 g) in a mixture of 10 mL of deionized water and 10 mL of diethyl ether. A mixture was stirred at room temperature for 48 hours. When the reaction was completed, the mixture was extracted with diethyl ether and dried over Na_2SO_4 and evaporated *in vacuo*. To the residue was crystallized by adding hexane. The solid was collected upon filtration, washed with cooled hexane and air-dried. Recrystallization from hexane to obtain white

crystal (80%), m.p. 66-68 °C, R_f 0.26 (1 : 1 EtOAc : Hexane); $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 7.35 (5H, s, Ar-H), 4.81 (2H, d), 3.75 (1H, dd), 3.221 (1H, d, -OH).

2.3 The general procedure for the oxidation of natural products.

Chromium(III) stearate (0.20 mmol) was added to substrate (5 mmol) in rounded bottom flask fitted with condenser. The mixture was dissolved in isooctane (5 mL) then, *tert*-butyl hydroperoxide; TBHP (18 mmol) as oxidant was added to give a purple suspension. The reaction mixture was heated at 70°C with stirring for 24 h. A color change was observed within 10 minutes in the case of every reaction. Upon completion or as indicated, the residue of chromium in reaction mixture was passed through short pad of cerite for GC analyzing and/or sometime dried over anhydrous MgSO_4 . The residue was purified by column chromatography on silica gel, eluting with ethyl acetate and/or hexane to give the desired product. The product yield was determined by GC. Some products could be chromatographed on silica gel. In general, however, concentrating samples led to undesired products or lowered yield due to volatility of the product.

2.3.1 3-oxo- α -ionone: yellow gum (37 %), R_f 0.30 (2:4, EtOAc : Hexane); $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 6.7 (1H, dd, $J = 9.5$ Hz), 6.15 (1H, d, $J = 15.7$ Hz), 6.00 (1H, s), 2.7 (1H, d, $J = 9.5$ Hz), 2.4 (1H, dd, $J = 16.8$ Hz), 2.30 (3H, s), 2.14 (1H, dd, $J = 16.8$ Hz), 1.92 (3H, s), 1.09 (3H, s), 1.02 (3H, s); $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)): 198.3 (1C, CO), 197.6 (1C, CO), 159.2 (1C), 143.6 (1C), 133.7 (1C), 126.8 (1C), 55.4 (1C), 47.3 (1C), 36.6 (1C), 27.8 (1C), 27.5 (1C), 27.3 (1C), 23.5 (1C).

2.3.2 4-oxo- β -ionone: yellow gum (41%), R_f 0.23 (2 : 4, EtOAc : Hexane); $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 7.2 (1H, d, $J = 16.52$ Hz), 6.2 (1H, d, $J = 16.51$ Hz), 2.53 (2H, t, $J = 6.86$ Hz), 2.35 (3H, s), 1.89 (2H, t, $J = 6.99$ Hz), 1.79 (3H, s), 1.24 (3H, s), 1.18 (3H, s); $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)): 198.7 (1C, CO), 197.6 (1C, CO), 157.9 (1C), 140.4 (1C), 133.5 (1C), 131.3 (1C), 37.2 (1C), 35.5 (1C), 34.1 (1C), 29.7 (1C), 27.9 (1C), 27.2 (1C), 13.4 (1C).

2.3.3 Acetophenone: light yellow liquid (98%), R_f 0.53 (1 : 4, EtOAc : Hexane); $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 7.99 (2H, d, $J = 7.06$ Hz), 7.58 (1H, t, $J = 7.37$ Hz), 7.49 (2H, t, $J = 7.74$ Hz), 2.64 (3H, s); $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)): 198.2 (1C, CO), 137.1 (1C), 133.1 (1C), 128.5 (2C), 128.5 (2C), 26.6 (1C).

2.3.4 Menthone: colorless liquid (78%), R_f 0.66 (100% CH_2Cl_2); $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 2.37(1H, m), 1.87-2.15 (6H, m), 1.40-1.77 (1H, m), 1.39 (2H, m), 1.00 (3H, d), 0.91 (3H, d), 0.85 (3H, d); $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)): 211.5 (1C, CO), 55.6 (1C), 50.7 (1C), 35.3 (1C), 33.8 (1C), 29.3 (1C), 27.7 (1C), 25.7 (1C), 22.1 (1C), 21.0 (1C), 18.5 (1C).

2.3.5 Cholestanone: white powder (58%), R_f 0.64 (1 : 4, EtOAc : Hexane); IR (KBr , cm^{-1}): 2868-2939 (s), 1710 (s), 1460 (s).

2.3.6 *p*-Cymene : colorless liquid (83%), R_f 0.59 (1 : 1, EtOAc : Hexane); $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 7.32 (4H, dd, $J = 8.32$ Hz), 3.07 (1H, m), 2.52 (3H, s), 1.45 (6H, d, $J = 7.10$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)): 126-146 (6Aromatic-C), 3.39 (1- CH_3), 24.2 (1- CH_3), 21.1 (1- CH_3).

2.4 Study on the optimum conditions for the oxidation catalyzed by chromium (III)stearate

2.4.1 Effects of chromium complexes

The oxidation reaction was conducted as described in general procedure using Cr(III)palmitate [29], Cr(III)stearate, Cr(III)behenate [29], Cr(III)acetylacetonate [29], Cr(III)Salen-Cl [31] as catalysts and in the absence of catalyst.

2.4.2 Effects of the amount of catalyst

The oxidation reaction was carried out as described in general procedure employed chromium(III) stearate as catalyst, but the different of amount of chromium(III)stearate was varied (0.01, 0.05, 0.10, 0.20, 0.25, 0.50 mmol).

2.4.3 Effects of the amount of oxidant

The oxidation reaction was carried out as described in general procedure employed chromium(III)stearate as catalyst, but the different amounts of TBHB were varied (9, 12, 18 ,20, 27 and/or 36 mmol).

2.4.4 Effects of temperature

The oxidation reaction was conducted as described in general procedure employed chromium (III) stearate as catalyst, but various reaction temperatures were varied (room temperature (30 °C), 50 °C, 70 °C and refluxing temperature (99 °C)).

2.4.5 Effects of type of oxidant on oxidation of cyclohexene

The oxidation reaction of cyclohexene was conducted as described in general procedure using Cr(III)salen-Cl as catalyst except for 50 mmol of cyclohexene being used and 80 %TBHP in organic solution was employed.

2.4.6 Effects of the amount of substrate on oxidation of cyclohexene

The oxidation reaction was conducted as described in general procedure using Cr(III)Salen as catalyst but the different of amount of substrate was varied (50 and10 mmol).

2.4.7 Effects of solvents

The oxidation reaction was conducted as described in general procedure employed Cr(III)stearate as catalyst, but the different solvents were varied (CH_2Cl_2 , CH_3CN , isooctane).

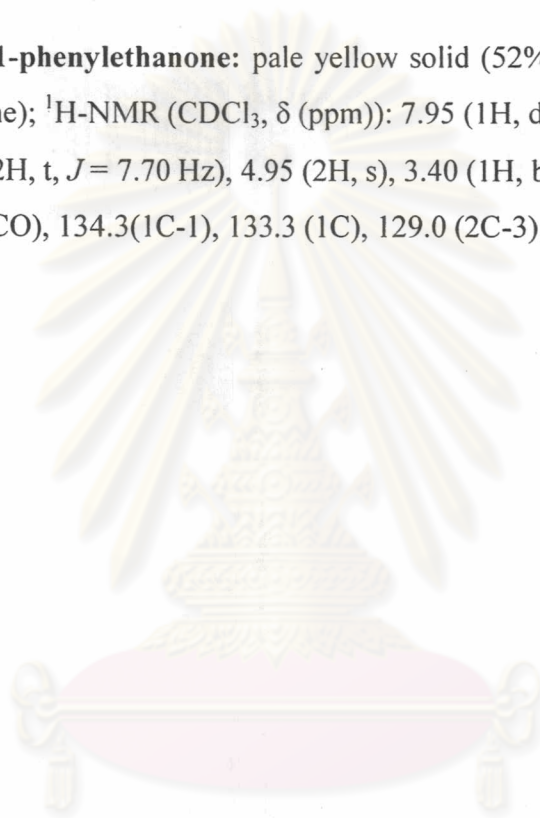
2.5 General procedure for the kinetic studies of oxidation reaction using gas chromatograph

The general oxidation procedure of substrate using chromium (III)stearate as catalyst was carried out. At different reaction time (1 to 12 h) an aliquot from the reaction mixture was taken, worked up and analyzed by GC.

2.6 Comparative study on the selective oxidation of primary alcohols in the presence of secondary ones

The selective oxidation reaction of 1-phenylethanol in the presence of 1-hexanol and benzyl alcohol, and 1-phenylethane-1,2-diol were conducted as described in general procedure using Cr(III)stearate as catalyst but the different amounts of oxidant (3 mmol and/or 9 mmol) was varied.

2-Hydroxy-1-phenylethanone: pale yellow solid (52%), m.p. 78-81°C; R_f 0.50 (1:1, EtOAc : Hexane); $^1\text{H-NMR}$ (CDCl_3 , δ (ppm)): 7.95 (1H, d, $J = 7.25$ Hz), 7.66 (2H, t, $J = 7.48$ Hz), 7.53 (2H, t, $J = 7.70$ Hz), 4.95 (2H, s), 3.40 (1H, br s); $^{13}\text{C-NMR}$ (CDCl_3 , δ (ppm)): 198.4 (1C, CO), 134.3(1C-1), 133.3 (1C), 129.0 (2C-3), 127.7 (2C), 65.4 (1C).



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