ออกซิเดชันของสารประกอบฟีนอลด้วยตัวเร่งปฏิกิริยาโลหะแทรนซิชันชิฟเบส

นายจิระศักดิ์ อิ่มอุไร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
หลักสูตรปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2545

ISBN 974-17-1082-8

OXIDATION OF PHENOLS BY TRANSITION METAL SCHIFF-BASE CATALYSTS

Mr. Jirasak Imurai

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Petrochemistry and Polymer Science
Program of Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2002

ISBN 974-17-1082-8

Thesis Title	Oxidation of Phenol by Transition Metal Schiff-base Catalysts
By	Mr. Jirasak Imurai
Field of Study	Petrochemistry and Polymer Science
Thesis Advisor	Assistant Professor Warinthorn Chavasiri, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master 's Degree

……Dean of Faculty of Science
(Associate Professor Wanchai Phothiphichitr, Ph.D.)

Thesis Committee

……Chairman
(Associate Professor Supawan Tantayanon, Ph.D.)

……Thesis Advisor
(Assistant Professor Warinthorn Chavasiri, Ph.D.)

……Member
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

……Member
(Assistant Professor Nuanphun Chantarasiri, Ph.D.)

……Member
(Nongnuj Muangsin, Ph.D.)

จิระศักดิ์ อิ่มอุไร : ออกซิเดชันของสารประกอบฟีนอลด้วยตัวเร่งปฏิกิริยาโลหะแทรนซิชันชิฟเบส (OXIDATION OF PHENOLS BY TRANSITION METAL SCHIFF-BASE CATALYSTS) อ. ที่ปรึกษา : ผศ.ดร.วรินทร ชวศิริ: 64 หน้า. ISBN 974-17-1082-8.

ออกซิเดชันของฟีนอลเร่งปฏิกิริยาด้วยสารประกอบเชิงซ้อนโลหะแทรนซิชันชิฟเบสภายใต้บรรยากาศออกซิเจน ได้เบนโซควิโนนที่สอดคล้องกันในปริมาณผลผลิตที่แตกต่างกันขึ้นอยู่กับหมู่แทนที่ของชิฟเบสลิแกนด์ และภาวะอื่นๆ ได้ศึกษาหาภาวะการเกิดปฏิกิริยาที่เหมาะสม ชนิดของตัวทำละลาย เวลา อุณหภูมิ ปริมาณและชนิดของตัวเร่งปฏิกิริยา ได้ศึกษาการออกซิไดซ์สารต้นแบบ 2,6-ไดเมทิลฟีนอลเป็น 2,6-ไดเมทิล-1,4-เบนโซควิโนนพบว่า ตัวเร่งปฏิกิริยา Co(II)-salen สามารถให้ผลิตภัณฑ์ที่ต้องการในปริมาณสูง (>80% ของผลผลิตที่แยกได้) ภายใต้ภาวะที่ไม่รุนแรง นอกจากนี้ภายใต้ภาวะที่ได้พัฒนาขึ้นนี้ พบว่าฟีนอลบางชนิดสามารถเปลี่ยนรูปเป็นเบนโซควิโนนที่สอดคล้องกันในปริมาณสูง

หลักสูตร...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่อนิสิต.....
สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์... ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา...2545... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4372235423 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD: SCHIFF-BASE / OXIDATION / PHENOLS
JIRASAK IMURAI : OXIDATION OF PHENOLS BY TRANSITION METAL SCHIFF-BASE CATALYSTS. THESIS ADVISOR : ASST. PROF. WARINTHORN CHAVASIRI, Ph.D.; 64 pp. ISBN 974-17-1082-8.

Metal-Schiff base complexes catalyze the oxidation of phenols with oxygen providing the corresponding benzoquinones in yield distribution majoring depending on the substitution mode of the Schiff base ligands and other conditions. The optimum conditions studied including type of solvents, reaction time, reaction temperature and the amount and type of catalyst were explored. The oxidation of a chemical model, 2,6-dimethylphenol to 2,6-dimethyl-1,4-benzoquinone was examined. It was found that Co(II)-salen catalyst provided the desired product in high yield (>80% isolated yield) under mild conditions. In addition, under this developed conditions, some phenols could be transformed to the corresponding benzoquinones in good yield.

Program...Petrochemistry and Polymer Science… Student's signature.....

Field of study…Petrochemistry and Polymer Science… Advisor's signature.....

Academic year……2002…… Co-advisor's signature…….

ACKNOWLEDGEMENTS

The author would like to express his gratitude to his advisor, Assistant Professor Dr.Warinthorn Chavasiri for providing valuable advice, encouragment and giving the asssistance throughout the course of this research. In addition, the author also wishes to express deep appreciation to Associate Professor Dr. Supawan Tantayanon, Assistant Professor Dr. Nuanphun Chantarasiri, Associate Professor Dr. Wimonrat Trakarnpruk and Dr. Nongnuj Jaiboon, serving as the chairman and members of his thesis committee, respectively, for their valuable suggestions and comments.

Appreciation is also extended to the Department of Chemistry and Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University for granting financial support to fulfill this study and provision of experimental facilities. The special thanks for permitting to use some equipments, especially, Natural Products Research Laboratory are acknowledged.

Further acknowledgement is extended to his friends for their help and encouragement during his graduate studies. Finally, the author is very appreciated to his family and his good friends whose names are not mentioned here for their love, assistance and encouragement throughout his entire education. Without them, the author would have never been able to achieve this goal.

CONTENTS

Page

CONTENTS (CONTINUE)

CONTENTS (CONTINUE)

Page

LIST OF FIGURES

Page

LIST OF TABLES

LIST OF TABLES (CONTINUE)

Page

LIST OF SCHEMES

Page

LIST OF ABBREVIATION

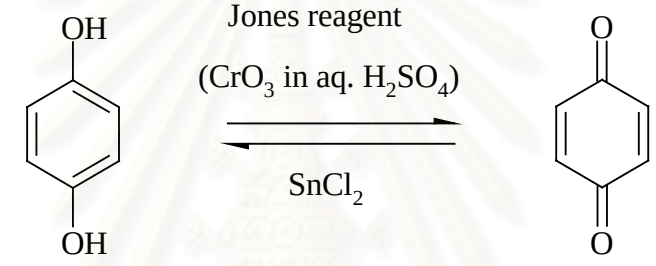
^{o}C	degree celsius
mmol	millimole
NMR	nuclear magnetic resonance
IR	infrared
g	gram (s)
mL	milliliter (s)
min	minute (s)
hr	hour (s)
cm^{-1}	unit of wavenumber
J	coupling constant
m	multiplet (NMR)
dd	doublets of doublet (NMR)
d	doublet (NMR)
s	singlet (NMR)
t	triplet (NMR)
m.p.	melting point
R_f	retardation factor
lit	literature
δ	chemical shift
w	weak (IR)
m	medium (IR)
s	strong (IR)
Hz	hertz

CHAPTER I

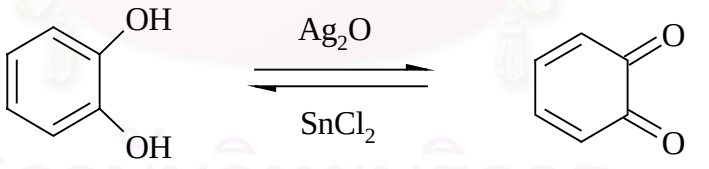
INTRODUCTION

1.1 Oxidation of phenols

Phenols are rather easily oxidized despite the absence of a hydrogen atom on the hydroxyl bearing carbon. Among the colored products derived from the oxidation of phenol by chromic acid is the dicarbonyl compound *para*-benzoquinone (also known as 1,4-benzoquinone or simply quinone); an *ortho* isomer is also known.[1-2]



hydroquinone *p*-benzoquinone



catechol *o*-benzoquinone

These compounds are easily reduced to their dihydroxybenzene analogs, and it is also from these compounds that quinones are best prepared. It should however be noted that *meta*-quinones having similar structures do not exist.

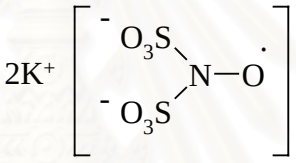
The redox equilibria between the dihydroxybenzenes or hydroquinone or catechol and their quinone oxidation states are so facile that milder oxidants than chromate (Jones reagent) are generally preferred. One such oxidant is Fremy's salt

($(KSO_3)_2NO$). Reducing agents other than stannous chloride (e.g. $NaBH_4$) may be used for the reverse reaction.

Although chromic acid oxidation of phenols having an unsubstituted *para*-position gives some *p*-quinone product, the reaction is complex and is not synthetically useful.

1.1.1 Oxidation of phenols with Fremy's radical

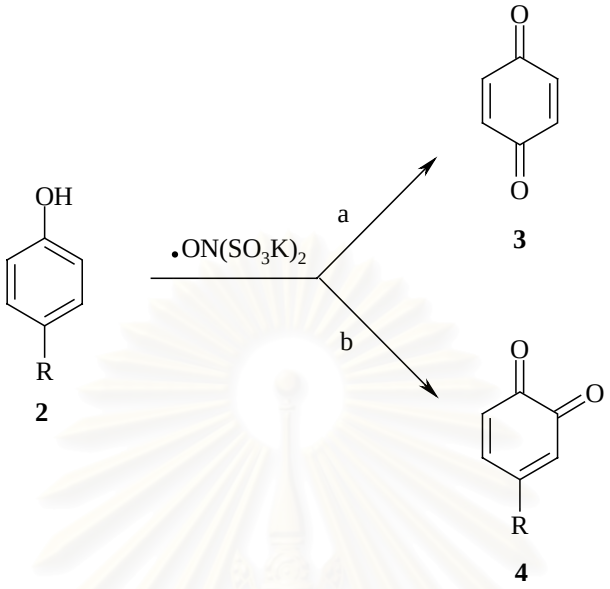
Fremy's radical or potassium nitrosodisulfonate (**1**); this salt selectively oxidizes phenols to corresponding quinones.[3-4] **1**, which in solution is represented by the structure that is rather unstable compound.[5-10] It oxidizes organic compounds, especially phenols, very easily and is generally very sensitive toward reduction.[11-14]



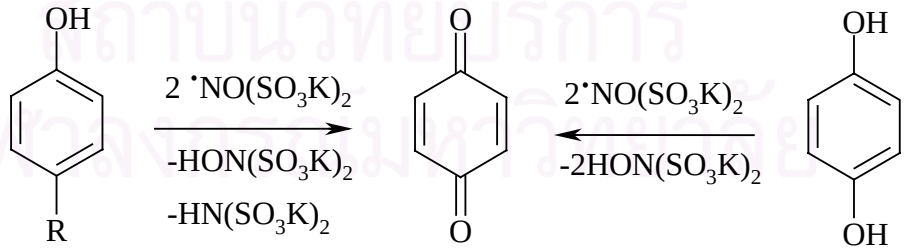
(1)

The oxidation of phenols with **1** represents an excellent synthetic method for the preparation of either *o*- or *p*-benzoquinone, under very mild conditions and usually in good yield.[2] The presence (or absence) of substituents on the aromatic ring, *para* to the hydroxy group, appears to control which kind of benzoquinone will be formed.

When the position *para* to the hydroxyl group in **2** is unsubstituted (R = H), *p*-benzoquinones **(3)** are formed (pathway a). If the position *para* to the hydroxyl group is substituented (R = OR, alkyl), oxidation leads to the formation of *o*-benzoquinones **(4)** (pathway b). One exception has been reported, namely when R = Cl. In this case, the oxidation proceeds, *via* pathway a, to form *p*-benzoquinones with the loss of chlorine.[2]



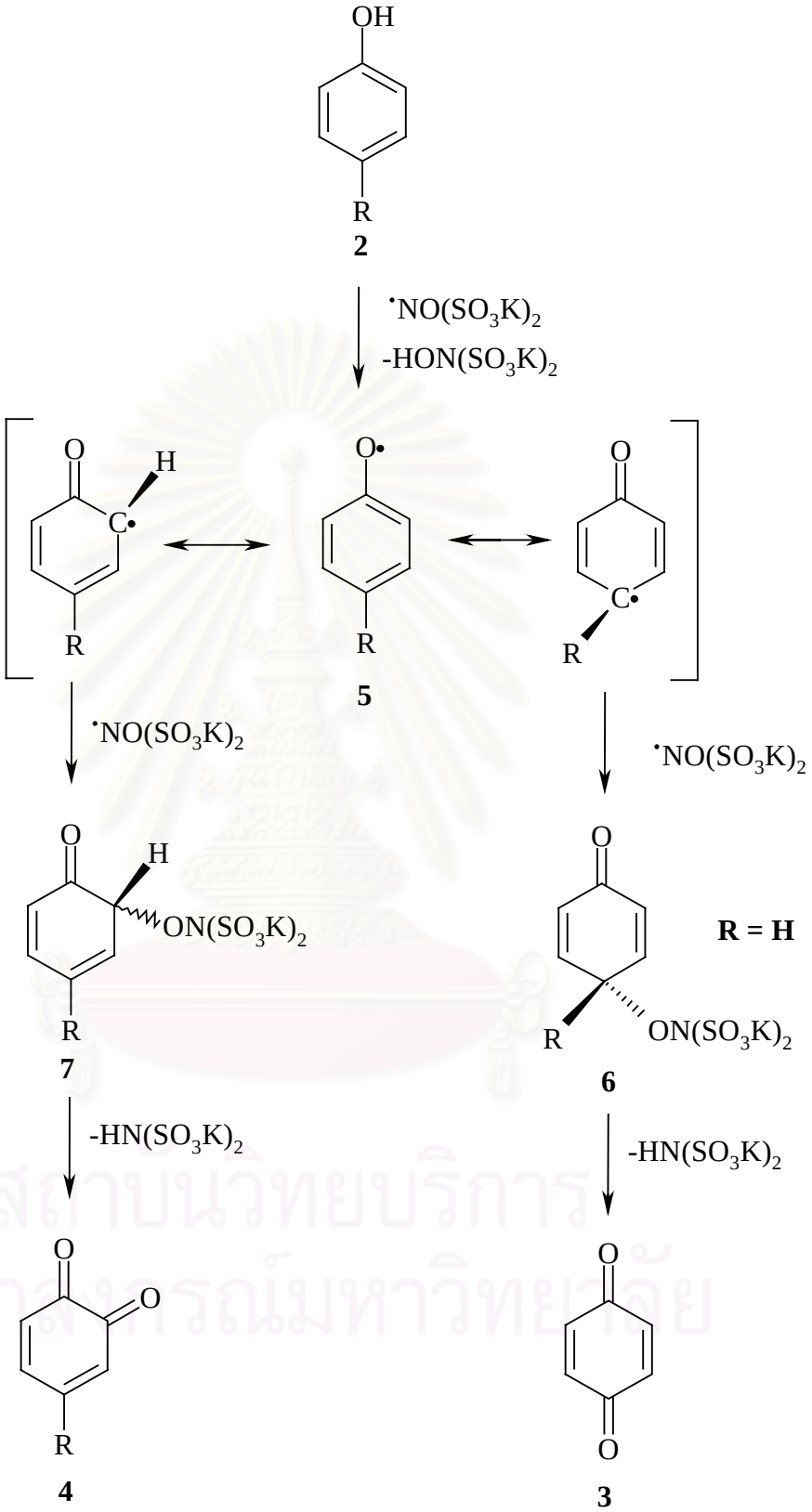
The mechanism of Fremy's radical oxidation has been extensively studied and has been fairly well established in the case of phenol. The overall stoichiometry of the oxidation of phenols has been shown to involve the reaction of 1 equiv of phenol with 2 equiv of **1** to give 1 equiv of benzoquinone, 1 equiv of dipotassium hydroxyimidodisulfate, and 1 equiv of dipotassium imidobisulfate. The oxidation of hydroquinones also results in the formation of benzoquinones, but the stoichiometry is different.



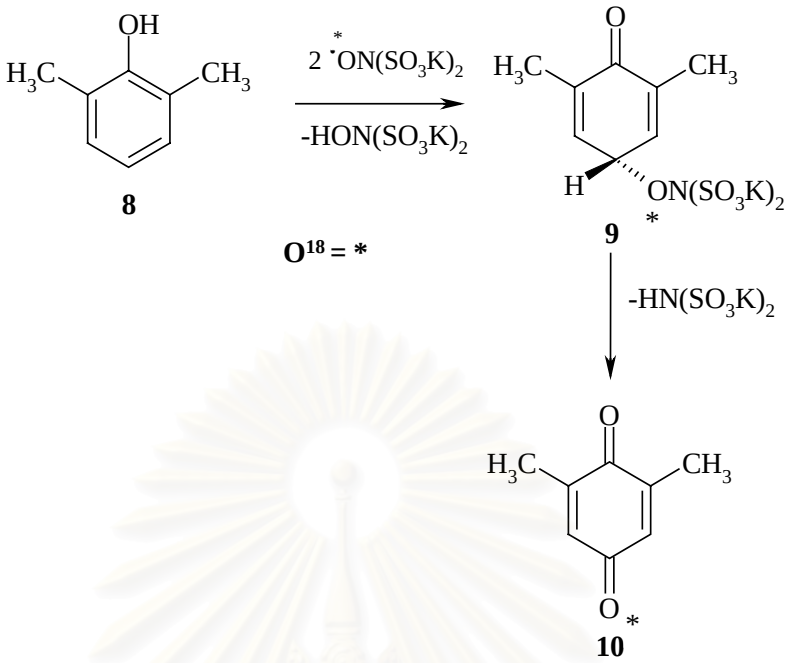
A general mechanistic interpretation, consistent with the observed stoichiometry, has been suggested for Fremy's radical oxidation of phenols and is depicted in Scheme 1.1.

Hydrogen abstraction from 2 by 1 results in the formation of dipotassium hydroxyimidobissulfate and the resonance stabilized phenoxy radical 5. This can then react with a second equivalent of 1 to give either cyclohexadienone intermidates 6 or 7, depending on nature of R followed by loss of elements of dipotassium imidodisulfate to give the benzoquinones 3 or 4.

The intermediacy of cyclohexadienones in Fremy's radical oxidations has been suggested, and if this were the case, the new oxygen atom which is incorporated into the quinone moiety should be derived from **1** and not from the solvent. This has been confirmed using ^{18}O-labeled **1**. 2,6-dimethylphenol **(8)** was oxidized with ^{18}O-labeled **1** (Scheme 1.2).[15] It was observed that 97% of the ^{18}O was incorporated as the new oxygen of the 2,6-dimethyl-1,4-benzoquinone **(10)**. Essentially no oxygen was incorporated from the solvent (*e.g.* ether, alcohol, or acetone) nor was there any exchange of the oxygen with the solvent.

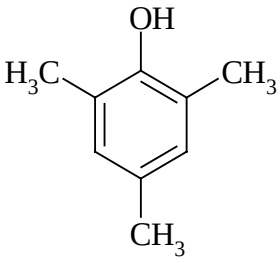


Scheme 1.1 The mechanism for the oxidation of phenols with Fremy's radical

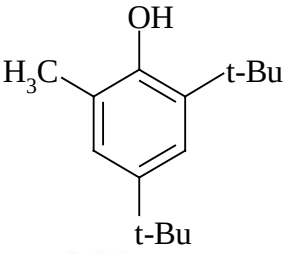


Scheme 1.2 The general mechanistic interpretation for Fremy's radical oxidation of phenols

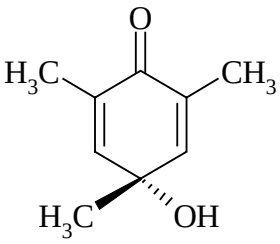
Further support for the intermediacy of cyclohexadienone in Fremy's radical oxidations was obtained from the study of the oxidation of 2,4,6-trialkylphenols. Oxidation of mesitol **(11)** or 4,6-di-*tert*-butyl-2-methylphenol **(12)** with **1** gave colorless solutions whose spectra were found to be very similar to that of 2,4,6-trimethyl-*p*-benzoquinols **(13,** 2,5-cyclohexadienone derivative**)** but differed from that of *o*-benzoquinols (2,4-cyclohexadienone derivatives).[16-17] Of the products that could be formed, **14-16**, only **15** should be colorless, whereas **14** and **16** would be yellow like other 2,4-cyclohexadienone derivatives.



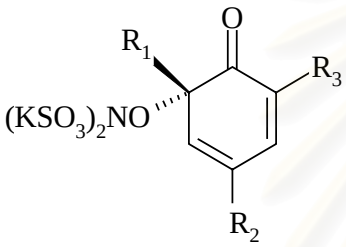
11



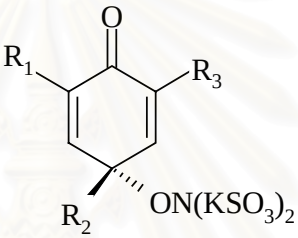
12



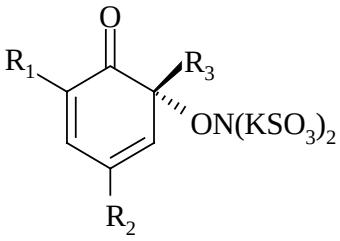
13



14a, b



15a, b



16a, b

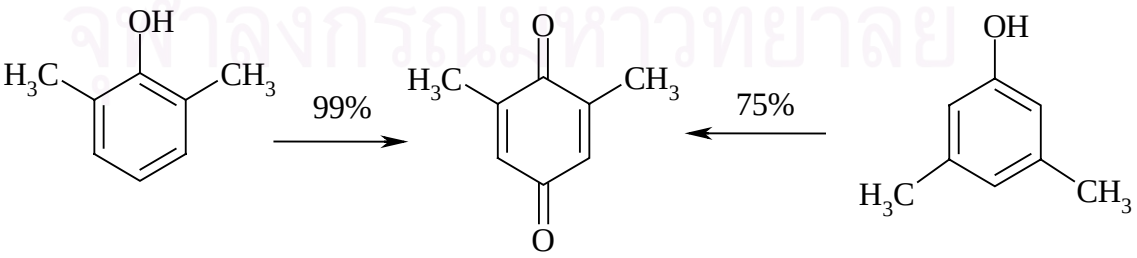
a, $R_1 = R_2 = R_3 = CH_3$

b, $R_1 = CH_3$; $R_2 = R_3$ = *tert*-butyl

.

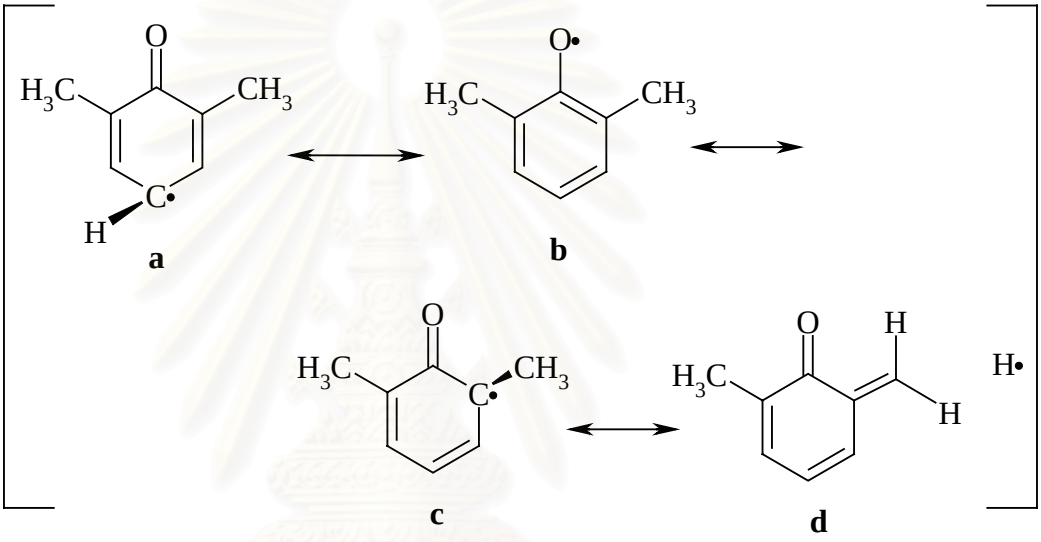
This indicates that the principal species in solution are 2,5-cyclohexadienones, although the presence of small amount of the 2,4-cyclohexadienone isomer could not be excluded.

In the oxidation of phenols with Fremy's radical, it can be seen from equation below that certain phenols, when oxidized by **1**, give rise to the same *p*-benzoquinone.



17 **19** **18**

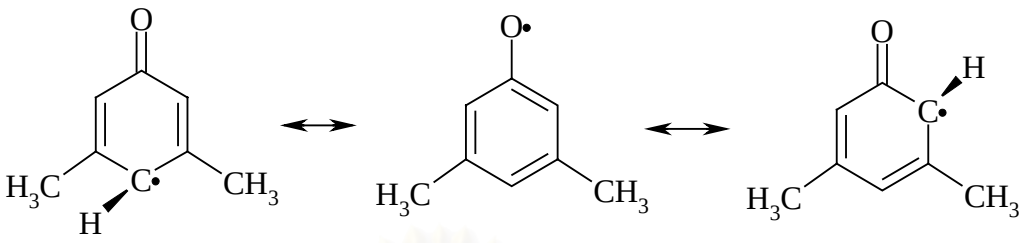
However, the yield of the quinones, formed the respective phenols, are significantly different. Both **17** and **18** are oxidized to **19,** the formation of **19** from **17** proceeds in 99% yield and whereas from **18** provides in 75% yield. Two factors appear to affect the extent of product formation: (1) electronic stabilization of the incipient phenoxy radical; and (2) steric requirements connected with the formation of the cyclohexadienone intermediates coresponding to **6** and **7**.



20

To illustrate this, radical **20** tends to be more stable than radical **21** because delocalization of the odd electron in **20** can occur adjacent to the methyl groups, as in **20c**, thus making additional stabilization through inductive and/ or hyperconjugative involvement of the methyl groups in **20d** possible. In the related structure **21**, the radical cannot be stabilized through such an involvement by the methyl groups.

Alternatively, the formation of cyclohexadienone intermediate, previously described, from **20a** is sterically more favorable than from **21a**. Consequently, there may be a significant difference in the yield of *p*-quinone, depending on which phenol is oxidized. Which effect, the electronic stabilization of the radical or the steric effect on the formation of the cyclohexadienone intermediate, is more important in Fremy's radical oxidations has not been quantitatively assessed.

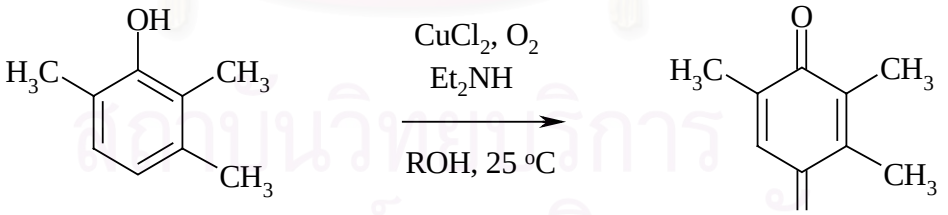


a **b** **c**

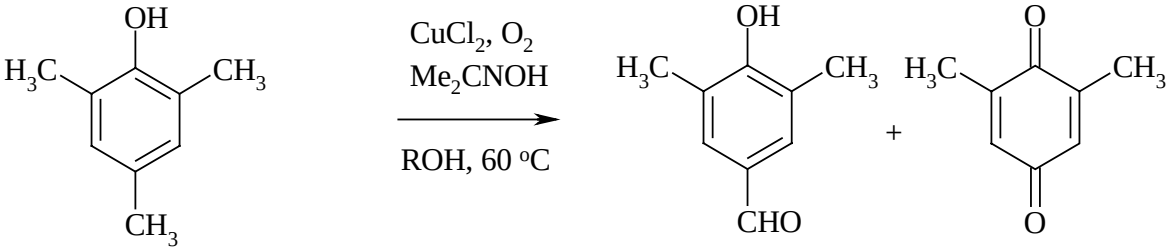
21

1.1.2 Oxidation of phenols with transition metals

In the presence of oxygen, copper(II) chloride converts phenol derivatives to various oxidation products. Depending on the reaction conditions, quinone and/or coupled compounds are formed.[18-19] Several groups have examined different sets of conditions employing $CuCl_2$ to favor either of these products. Thus, 2,3,6-trimethylphenol **(22)** was selectively oxidized to trimethyl-*p*-benzoquinone **(23)** with $CuCl_2$/amine/O_2 as the catalyst, while 2,4,6-trimethylphenol **(24)** was converted to 3,5-dimethyl-4-hydroxybenzaldehyde **(25)** using a catalytic system employing either acetone oxime or amine.[20-21]

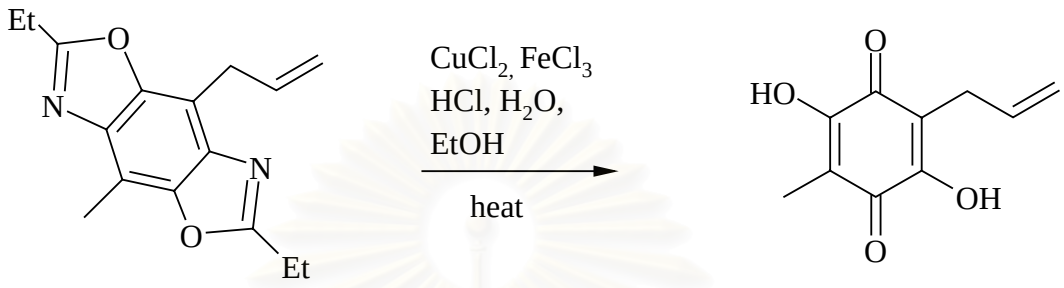


22 **23**



24 **25** **26**

The oxidation of alkoxyphenols **(27)** to the corresponding quinones (**28)** has been studied, and even benzoxazole derivative can be oxidized by a mixture of copper (II) chloride and iron(III) chloride.[22-23]



27 **28**

1.1.3 Oxidation of phenols with metal Schiff base catalysts

Synthetic reversible oxygen-carrying chelates[24-25], *i.e.*, chelates that can take up and release molecular oxygen reversibly, have been of interest as model compounds in the study of the reversible oxygenation mechanisms involved in the very complex natural oxygen carriers[26], *e.g.* the hemoglobins and hemocyanins, and as a means of separating molecular oxygen from the air.

The example of a synthetic reversible oxygen-carrying chelates; metal Schiff base complexes were prepared in 1933 by Pfeiffer, Breith, Lubbe and Tsumaki, but no study involved in catalytic properties. For several years ago the study of these types of complexes in catalytic properties were developed and found that it can be used as a catalyst for the oxidation reaction in organic synthesis.

Literature review on metal Schiff base-catalyzed oxidation of phenols

The development of new process for the oxidation of phenols continues to be an important goal for both academic and industrial point of view. Generally the process of the functionalization of phenols to quinones must work under hard conditions and the selectivity of reaction is normally low. Metal Schiff base complexes have been reported to be employed as catalyst in the functionalization of quinones under mild conditions.

In 1984 Wakamatsu and colleagues reported that 1,5-dihydroxynaphthalene and its derivatives can be oxidized by molecular oxygen in the presence of catalytic amounts of salcomine under neutral conditions to afford the corresponding 1,4-naphthoquinone as major product.[27]

In 1995 Bozell and Hames reported that *para*-substituted phenolics were oxidized to the coresponding benzoquinone with oxygen in the presence of catalytic amounts of Co(II)-Schiff base complexes. The reaction products observed were found to depend on the structure of catalyst. The 5-coordinate catalysts (pyridine)[bis (salicylidene)ethylenediamine)cobalt] [(pyr)Co(salen)] and [bis-((salicylideneamino) ethy)amine]cobalt [Co(*N*-Me salpr)] could convert 3,5-dimethoxy-4-hydroxybenzyl alcohol to 2,6-dimethoxybenzoquinone in high yield. However, the 4-coordinate Co(II)-salen converts 3,5-dimethoxy-4-hydroxybenzaldehyde to 2,6-dimethoxybenzoquinone in 72% isolated yield while it is unreactive with 5-coordinate catalysts.[28]

In 1996 Maruyama and coworker reported that Co(II)salen was used as catalyst in the oxidation of 2,4- and 2,6-di-*tert*-butylphenols bearing an unsaturated side chain, with *tert*-butyl hydroperoxide (TBHP) in CH_2Cl_2 at room temperature. The formation of *tert*-butyl peroxylated products was predominant. The position of *tert*-butyl peroxylation depends on the nature of the unsaturated side chain.[29]

1.2 The goal of this research

The purposes of this research can be summarized as follows:

1 To synthesize Schiff base ligands.

2 To synthesize transitions metal Schiff base complexes.

3 To study the optimum conditions for 2,6-dimethylphenol oxidation by using transition metal Schiff base complexes.

4 To study the capability of catalyst for the oxidation of other phenols under optimum conditions.

CHAPTER II

EXPERIMENTAL

2.1 General procedure

Melting points were determined with a Fishers-Johns melting point apparatus and are uncorrected. The FT-IR spectra were recorded on a Nicolet Fourier Transform Infrared Spectrophotometer model Impect 410. Solid samples were incorporated to potassium bromide to form pellet. The ^{1}H and ^{13}C-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) solution, with a Bruker model ACF200 spectrometer and Jeol, model JNM-A500.

Chromatography: thin layer chromatography (TLC) was carried out on aluminium sheets precoated with silica gel (Merck's, Kieselgel 60 PF_{254}). Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G). Gas chromatography analysis was carried out on a Shimadzu Gas Chromatograph GC-9A instrument equipped with flame ionization detector with N_2 as carrier gas. The column used for gas chromatography was Carbowax 20M.

2.2 Chemicals

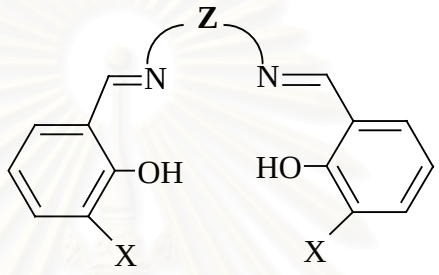
All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades. The reagents used for synthesizing Schiff base ligands, metal Schiff base complexes and all phenols were purchased from Fluka chemical company and were used without further purification. Merck's silica gel 60 G Art 7734 (70-230 mesh) was used as adsorbent for column chromatography.

2.3 Syntheses

2.3.1 Schiff base ligands

General procedure[30]

An interested aldehyde or ketone (1 or 2 mol-equiv) was slowly added to a solution of primary diamines (1 mol-equiv) in methanol. The solution was stirred at room temperature until precipitate occurred. The precipitate was filtered off and recrystallized by an appropriate solvent.



a X = H, Z = -CH_2CH_2- **f** X = H, Z = -(*o*-C_6H_3-4-NO_2)-

b X = H, Z = -$CH_2CH_2CH_2$- **g** X = H, Z = -(2,6-C_5H_3N)-

c X = H, Z = -(*o*-C_6H_{10})- **h** X = OMe, Z = -CH_2CH_2-

d X = H, Z = -(*o*-C_6H_4)- **i** X = OMe, Z = -(*o*-C_6H_4)-

e X = H, Z = -(*m*-C_6H_4)-

***Bis*(salicylaldehyde)*N,N'*-ethylenediimine[30] (salen, a):** Bright yellow crystals 96% yield; m.p. 124-125 ^oC; R_f 0.74 (silica gel: dichloromethane); IR (KBr): 3500 (w), 3010-3050 (w), 2870-2950 (w), 1750-2000(w), 1640 (s), 1450-1600 (s), 1280 (s) and 1170 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.84 (s, 4H), 6.83 (dt, J = 7.48, 1.22, 2H), 6.93 (d, J = 8.24, 2H), 7.18 (dd, J = 7.78, 1.53, 2H), 7.26 (dt, J = 7.78, 1.53, 2H), 8.29 (s, 2H) and 13.2 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 59.5 (2C), 116.8 (2C), 118.5 (2 x 2C), 131.4 (2C), 132.2 (2C), 160.9 (2C) and 166.3 (2C).

***Bis*(salicylaldehyde)*N,N′*-trimethylenediimine[31] (saltn, b):** Yellow needle crystals 24% yield; m.p. 51-52 ^{o}C; R_f 0.33 (silica gel: dichloromethane); IR (KBr): 3420 (w), 3080-3020, 2950-2860 (w), 1640 (s), 1625, 1580, 1500 (m), 1450 (m), 1290 (m) and 760 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.05-2.10 (quintet, 2H, J=6.71), 3.66-3.69 (dt, J=6.72, 0.92), 6.85-7.31 (m, 8H), 8.33 (s, 2H) and 13.42 (s, 2H). ^{13}C-NMR ($CDCl_3$) δ (ppm): 31.6 (C), 56.7 (2C), 116.9 (2C), 118.5 (2C), 118.7 (2C), 131.2 (2C), 132.2 (2C), 161.0 (2C) and 165.3 (2C).

***Bis*(salicylaldehyde)*N,N′*-cyclohexane-1,2-diimine[30] (salcycloen, c):** Bright yellow crystals 82% yield; m.p.109-110 ^{o}C; R_f 0.68 (silica gel: dichloromethane); IR (KBr): 2997-3071 (w), 2864-2931 (w), 1625 (s), 1536 (s), 1452 (s) and 749 (s) cm^{-1}.

***Bis*(salicylaldehyde)*N,N′*-*o*-phenylenediimine[30] (sal-*o*-phen, d):** Orange needle crystals 82% yield; m.p.164-165 ^{o}C; R_f 0.80 (silica gel: dichloromethane); IR (KBr): 3500 (w), 3050 (w), 2870-2950 (w), 1630 (s), 1560-1485 (s), 1275 (s) and 1190 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.85 (t, J = 7.32 Hz, 2H), 7.02 (d, J = 13.24 Hz, 2H), 7.20 (m, 4H), 7.31 (m, 2H), 7.35 (m, 2H), 8.60 (s, 2H) and 13.0 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 117.5 (2C), 118.9 (2C), 119.1 (2C), 119.6 (2C), 127.7 (2C), 132.3 (2C), 133.3 (2C), 142.4 (2C), 161.3 (2C) and 163.6 (2C).

***Bis*(salicylaldehyde)*N,N′*-*m*-phenylenediimine[31] (sal-*m*-phen, e):** Orange needle crystals 73% yield; m.p.160 ^{o}C; R_f 0.80 (silica gel: dichloromethane); IR (KBr): 3500 (w), 3050 (w), 2870-2950 (w), 1630 (s), 1600-1450 (s), 1300 (s) and 1190 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.84 (t, J = 7.29, 2H), 7.02 (d, J = 13.24, 2H), 7.20 (m, 4H), 7.33 (m, 2H), 7.40 (m, 2H), 8.64 (s, 2H) and 13.1 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 117.3 (2C), 118.5 (2C), 119.2 (2C), 119.6 (2C), 127.7 (2C), 132.3 (2C), 133.3 (2C), 142.4 (2C), 161.3 (2C) and 163.5 (2C).

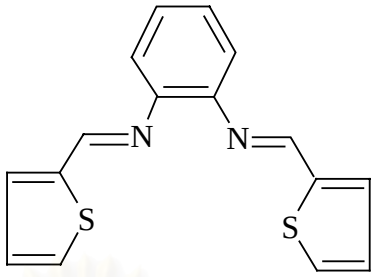
***Bis*(salicylaldehyde)*N,N′*-(4-nitro)-1,2-phenylenediimine[31] (sal-(4-nitro)-*o*-phen, f):** Orange-yellow needle crystals 24% yield; m.p. 210 ^{o}C; R_f 0.94 (silica gel: dichloromethane). IR (KBr): 3700-3300 (w), 3100-3050(w), 1620(s), 1570-1480(s), 1480(s), 1570-1350(s), and 1280(s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.93-7.69 (m, 10H), 8.36-8.34(m, 2H), 9.08-8.98 (d, J=5.5, 1H), and 12.53-12.64 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 116.0 (4C), 123.3 (2C), 117.8 (1C), 117.9 (2C), 120.2 (2C),122.0 (2C), 134.9 (3C), 167.9 (2C) and 168.2 (2C).

***Bis*(salicylaldehyde)*N,N′*-pyridine-2,6-diimine[31] (sal-py-2,6-diimine, g):** Orange crystals 53% yield; m.p. 183.0-185.0 ^{o}C R_f 0.88 (silica gel: dichloromethane). IR (KBr): 3100-3000 (w), 1630-1600 (s), 1600-1450 (s), and 1280 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.52-8.29 (m, 11H9.70 (s, 2H), and 13.25 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 117.7 (2C), 119.8 (2C), 120.0 (2C), 134.1 (2C), 134.7 (1C), 136.0 (4C), 142.2 (2C), 162.7 (2C) and 166.8 (2C).

***Bis*-(*o*-vanillin) *N,N′*-ethylinediimine[32] (salen OMe, h):** Yellow needle 97% yield; m.p. 163-165 ^{o}C R_f 0.58 (silica gel : dichloromethane). IR (KBr): 3500 (w), 3050 (w), 2840-2990 (w), 1630 (s), 1465 (s), 1255 (s) and 1080 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.88 (s, 6H), 3.94 (s, 4H), 6.77 (t, J = 7.63, 2H), 6.84 (dd, J = 7.94, 1.53, 2H), 6.90 (dd, J = 7.94, 1.52, 2H), 8.32 (s, 2H) and 13.6 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 56.0 (2C), 59.4 (2C), 114.1 (2C), 118.0 (2C), 118.4 (2C), 123.1 (2C), 148.3(2C), 151.4 (2C) and 166.6 (2C).

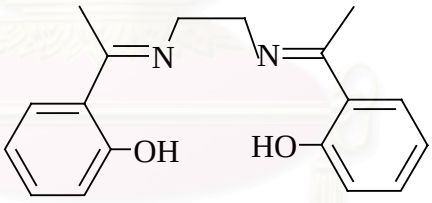
***Bis*(3-methoxysalicylaldehyde)-*o*-phenylenediimine[30] (3-OMe sal-*o*-phen, i):** Orange product 70 % yield; m.p. 168-170 ^{o}C R_f 0.26 (silica gel : dichloromethane). IR (KBr): 3500(w), 3050 (w), 2828-2959 (w), 1611 (s), 1465 (s), 1254 (s) and 1072 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.9 (s, 6H), 6.9-7.3 (m, 10H), 8.7 (s, 2H) and 13.2 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 56.0 (2C), 59.4 (2C), 114.1 (2C), 118.0 (2C), 118.4 (2C), 123.1 (2C), 148.3(2C), 151.4 (2C) and 166.6 (2C).

***N,N′-1, 2*-phenylene *bis*(2-thenylideneimine)[33] (thiophen-*o*-phen, j):** Yellow needles 62 % yield; m.p. 148-149 ^{o}C (lit. m.p. 148 ^{o}C); R_f 0.68 (silica gel: ethanol); IR (KBr) 3090-3050 (w), 2950 (w), 1630 (w) and 1225 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.70 (s, 2H), 6.86 (dd, J = 3.36, 1.22, 1H), 6.94 (t, J = 4.43, 1H), 7.13 (t, J = 4.27, 1H), 7.23 (dd, J = 4.89, 1.23, 1H), 7.29 (m, 2H), 7.37 (dd, J = 7.32, 1.22, 1H); 7.47 (dd, J = 3.82, 1.22, 1H), 7.51 (dd, J = 5.03, 1.22, 1H) and 7.83 (dd, J = 6.87, 1.83, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 44.0 (1C), 109.9 (1C), 119.9 (1C), 123.0 (1C), 123.3 (1C), 125.2 (1C), 125.4 (1C), 127.2 (1C), 127.9 (1C), 128.0 (1C), 128.9 (1C), 131.8 (1C), 135.8 (1C), 138.8 (1C), 143.0 (1C) and 147.6 (1C).



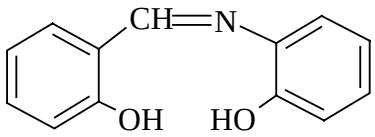
(j)

***Bis*(2-hydroxyacetophenone)*N,N′*-ethylenediimine[30] (Me salen, k):** Yellow needle crystals 81% yield; m.p. 200-201 ^{o}C; R_f 0.70 (silica gel: dichloromethane); IR (KBr) 3500 (w), 3010-3050 (w), 3080 (w), 2870-9509 (w), 1800-2000 (w), 1620 (s), 1450-1600 (s), 1220 (s) and 1180 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.37 (s, OH), 3.97 (s, 4H), 6.78 (dt, J = 7.70, 1.28, 2H), 6.91 (dd, J = 8.55, 1.28, 2H), 7.27 (dt, J = 7.91, 1.8, 2H), 7.52 (dd, J = 7.91, 1.50, 2H) and 15.80 (s, 2H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 14.7 (2C), 50.2 (2C), 117.4 (2C), 118.5 (2C), 119.4 (2C), 128.1 (2C), 132.4 (2C), 163.1 (2C) and 172.7 (2C).



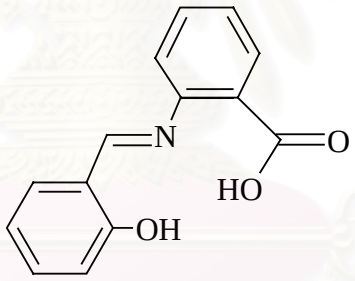
(k)

***N*-salicylalidene-aminophenol[34] (salop, l):** Red needles 79 % yield; m.p. 189-190 ^{o}C; R_f 0.64 (silica gel: dichloromethane); IR (KBr) 3500 (w), 3050 (w),1640 (s), 1450-1600 (s), 1280 (s) and 1150 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 5.79 (s, 1H), 6.95-7.09 (m, 4H), 7.15 (dd, J = 7.79, 1.53, 1H), 7.22 (dt, J = 7.94, 1.53, 1H), 7.04-7.45 (m, 2H), 8.69 (s, 1H) and 12.25 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 115.9 (1C), 117.3 (1C), 118.3 (1C), 119.3 (1C), 119.6 (1C), 121.0 (1C), 128.8 (1C), 132.7 (1C), 133.7 (1C), 136.8 (1C), 149.9 (1C), 160.6 (1C) and 164.0 (1C).



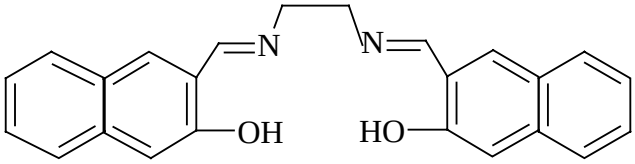
(l)

***N*-salicylalidene-*o*-aminobenzoic acid**[35] **(saloa, m):** Red crystals 57% yield; m.p. 203-205 ^{o}C; R_f 0.75 (silica gel: ethanol); IR (KBr) 3500 (w), 3050-3100 (w), 1620 (s), 1460-1580 (s) and 1240 (s) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.50 (s, 1H), 6.66 (d, J = 8.54, 0.91, 1H), 6.67 (dd, J = 8.53, 1.22, 1H), 6.99 (d, J = 8.55, 1H), 7.03 (dd, J = 7.33, 0.92, 1H), 7.30 (dd, J = 7.78, 1.52, 1H), 7.52 (dt, J = 7.64, 1.83, 1H), 7.56 (dd, J = 7.78, 1.53, 1H), 7.90(dd, J = 8.39, 1.83, 1H), 9.90 (s, 1H) and 11.00 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 114.5 (1C), 116.3 (1C), 117.2 (1C), 119.0 (2C), 119.4 (1C), 130.4 (1C), 131.1 (1C), 133.6 (1C), 136.4 (1C), 151.5 (1C), 160.7 (1C), 169.6 (1C) and 191.8 (1C).



(m)

***Bis*(2-hydroxy-1-naphthaldehyde)*N,N′*-ethylenediimine (*Bis*(nap), n):** Yellow crystals 69 % yield; m.p. 309 ^{o}C. R_f 0.26 (silica gel: ethyl acetate); IR (KBr): 3053 (w), 1649 (s), 1499-1546 (s), 1212 (s) and 1000 (s) cm^{-1}.



(n)

2.3.2 Metal complexes

- **[Cr(III)-(salen)(H_2O)$_2$]Cl**[36]

To a solution of chromium (III) chloride hexahydrate 26.65 g (0.1 mol) in ethylene glycol-water-methanol (1:1:3, 300 mL) were added salicylaldehyde 24.42 g (0.2 mol) and ethylenediamine 6.01 g (0.1 mol). After the mixture was heated at about 110 ^{o}C for about 30 min, sodium carbonate (0.06 mol) was added in small portions to the solution, followed by refluxing of the solution for about 3 to 4 hr. On concentrating the solution, a reddish brown precipitate was obtained. The precipitate was recrystallized from 80% methanol to give reddish orange crystals of the desired complex 19.6 g (50 % yield). The crystals are highly soluble in methanol and ethanol, fairly soluble in water, and almost insoluble in benzene and diethyl ether.

- **VO(IV)-salen**[37]

The complex VO(acac)$_2$ 4.35 g (16.4 mmol) was added to acetonitrile 150 mL and the mixture was heated to reflux . Salen 5.07 g (16.40 mmol) was added to the hot fitrate using a Soxhlet extractor. The mixture was keep at reflux temperature for 30 min, then cooled. After 1 day the green needle of VO(IV)-salen 2.65 g (49 % yield) was filtered off, washed with cold acetonitrile and diethyl ether, and dried *in vacuo*, m.p. 168.5 ^{o}C; IR (KBr): 3500 (w), 3020 (w) and 1620 (s).

- **Co(II)-salen, Co(II)-saltn, Co(II)-salcycloen, Co(II)-(3-OMe sal-*o*-phen), Co(II)-sal-*m*-phen, Co(II)-sal(4-nitro)-*o*-phen, Co(II)-sal-py-2,6-diimine, Co(II)-*Bis*(nap) and Ni(II)-salen**[37]

Salen 2.7 g (0.01 mol) was dissolved in ethanol 50 mL at 70 ^{o}C. After stirring the solution until homogeneity, metal(II)acetate (0.01 mol) dissolved in ethanol was dropped slowly and refluxed for 1 hr. Precipitate of metal salen complex had occurred. The products were filtered and washed with cold ethanol.

Co(II)-salen: yield 68 %, m.p. 228.5 ^{o}C: IR (KBr): 3500 (w), 3020 (w) and 1640 (m).

Co(II)-saltn: yield 60 %, m.p. 389 ^{o}C: IR (KBr): 3500 (w), 3020 (w) and 1640 (m).

Co(II)-salcycloen: yield 56 %, m.p. 349 ^{o}C: IR (KBr): 3500 (w), 3025 (w) and 1602 (m).

Co(II)-(3-OMe sal-o-phen): yield 46 %, m.p. 262 ^{o}C: IR (KBr): 3500 (w) and 1603 (m).

Co(II)-sal-m-phen: yield 46 %, m.p. 220 ^{o}C (dec): IR (KBr): 3500 (w, 3071 (w) and 1607 (m).

Co(II)-sal(4-nitro)-o-phen: yield 49 %, m.p. >400 ^{o}C: IR (KBr): 3500 (w), 3050 (w) and 1612 (m).

Co(II)-sal-py-2,6-diimine: yield 66 %, m.p. 279 ^{o}C (dec): IR (KBr): 3500 (w), 3071 (w) and 1578 (m).

Co(II)-Bis(nap): yield 45 %, m.p. 380 ^{o}C (dec): IR (KBr): 3500 (w), 3053 (w) and 1621 (m).

Ni(II)-salen: yield 96 %, m.p. 140 ^{o}C: IR (KBr): 3500 (w), 3020 (w) and 1610 (m).

- Cu(II)-salen and Mn(II)-salen[37]

Salen 2.7 g (0.01 mol) was dissolved in *N,N'*-dimethylformamide (DMF) 30 mL at 60 ^{o}C. After stirring the solution until homogeneity, metal(II)acetate (0.01 mol) dissolved in DMF was dropped slowly and precipitation of metal salen complexes had occurred. The products were filtered and washed with acetone.

Cu(II)-salen: yield 92 %, m.p. 297 ^{o}C: IR (KBr): 3500 (w), 3015 (w) and 1620 (s).

Mn(II)-salen: yield 94 %, m.p. 297 ^{o}C: IR (KBr): 3500 (w), 3060 (w) and 1620 (s).

- Cr(III)-(salen).NO_3

This complex was prepared employing a similar method to that described for Co (II)-salen by using salen 2.7 g (0.01 mol) and chromium(III) nitrate nonahydrate (0.01 mol) and recrytallized by 95 % ethanol-dichlomethane; the pale orange solid was obtained.

Cr(III)-salen.NO_3: yield 33 %, m.p. 188-189 ^{o}C: IR (KBr): 3500 (w), 3020 (w) and 1600 (s).

- Fe(II)-salen[37]

This complex was prepared employing a similar method to that described for Co-(II)-salen by using salen 2.7 g (0.01 mol) and iron(II) sulfate (0.01 mol) and

recrystallized by 95 % ethanol-dichloromethan. The dark brown solid of Fe(II) salen was obtained.

Fe(II)-salen: yield 18 %, m.p. 198-200 ^{o}C: IR (KBr): 3500 (w), 3020 (w) and 1620 (s).

- Co(II)-sal-*o*-phen[30]

This complex was prepared utilizing the same methodology as that described for the preparation of Co(II)-salen using sal-*o*-phen 3.2 g (0.01 mol) and cobalt(II)-acetate (0.01 mol). The brown powder of Co(II)-sal-*o*-phen 1.10 g was obtained (29 % yield); m.p. 165 ^{o}C; IR (KBr): 3500 (w), 3015 (w) and 1610 (s).

- Co(II)-(Me salen), Co(II)-salop, Co(II)-saloa, Co(II)-(salen OMe), Co(II)-thiophene-*o*-phen

The general procedure for the preparation of the following metal complexes are described as follows: an ethanol (80 mL; 95 %) solution of ligand (10 mmol) was mixed with an aqueous (80 mL) solution of cobalt(II) chloride hexahydrate (10 mmol). Then a solution (42 mL) of $CH_3COONa.3H_2O$ (30 mmol) was added and refluxed for 2-3 hr. After that the solution was cooled for overnight and metal Schiff base complexes were obtained.

The green needles of Co(II)-(Me salen) were obtained 1.98 g (56% yield); m.p.260 ^{o}C; IR (KBr): 3500 (w), 3020 (w) and 1610 (s).

The yellow powder of Co(II)-salop was obtained 2.16 g (80% yield); m.p. >300 ^{o}C; IR (KBr): 3500 (w), 3020 (w) and 1605 (s).

The gold solid Co(II)-(salen OMe) was obtained 1.48 g (45% yield); m.p. >300 ^{o}C; IR (KBr): 3500 (w, 3050 (w) and 1610 (s).

2.4 Study on the optimum conditions for the oxidation of phenols

2.4.1 General procedure

To a solution of phenols (1.0 mmol) in dimethylformamide (DMF) (10 mL) containing metal Schiff base (0.1 mmol) in a round bottom flask with a balloon filled with oxygen (O_2). The mixture was stirred for 5 hr at room temperature. After the reaction was completed, 1 mL of reaction mixture was taken and extracted with diethyl ether. The combined extracts were washed with 25 %H_2SO_4 solution and saturated solution of $NaHCO_3$ respectively. The organic layer was dried over

anhydrous Na_2SO_4 and analyzed by GC with the addition of an exact amount of an appropriate internal standard.

2.4.2 Effect of metal salen

The oxidation reaction was carried out in the same manner as previously described employing eight metal salen complexes : Co(II)-salen, Ni(II)-salen, Cr(III)-salen.Cl, Cr(III)-salen.NO_3, VO(IV)-salen, Cu(II)-salen, Mn(II)-salen and Fe(II)-salen.

2.4.3 Effect of cobalt salts and complexes

The oxidation reaction was carried out in the same manner as aforementioned, but Co-salen, Co-(acetate)$_2$.4H_2O, Co-Cl_2.6H_2O, Co-(acac)$_2$.4H_2O, Co-(stearate)$_2$ and Co-(palmitate)$_2$ were used instead of metal Schiff base complexes.

2.4.4 Effect of Co(II)-Schiff base complexes

The oxidation reaction was carried out in the same manner as described above, but Co(II)-salen, Co(II)-saltn, Co(II)-salcycloen, Co(II)-(3-OMe sal-*o*-phen), Co(II)-sal-*m*-phen, Co(II)-sal(4-nitro)-*o*-phene, Co(II)-sal-py-2,6-diimine, Co(II)-*Bis*(nap), Co(II)-sal-*o*-phen, Co(II)-(Me salen), Co(II)-salop, Co(II)-saloa, Co(II)-(salen OMe) and Co(II)-thiophene-*o*-phen were used instead of metal Schiff base complexes.

2.4.5 Effect of amount of catalyst (Co(II)-salen)

The oxidation reaction was carried out as previously described but amount of catalyst was varied : 0, 0.02, 0.05, 0.10, 0.15, 0.20 and 0.30 mmol.

2.4.6 Effect of solvents

The oxidation reaction was carried out in the same manner as aforementioned, except for that ethanol, acetonitrile, acetone, methanol, 1,2-dichloroethane, THF, dichloromethane, chloroform, pyridine and carbontetrachloride were employed instead of DMF.

2.4.7 Effect of the amount of solvent

The oxidation reaction was carried out as previously described, but the amount of solvent was varied: 3, 5, 10, 20 and 30 mL.

2.4.8 Effect of temperature

The oxidation reaction was carried out in the same manner as aforementioned, but temperature was varied: 45 and 60 ^oC.

2.4.9 Effect of oxidants

The oxidation reaction was carried out as previously described, except for that no oxidant, air, oxygen (bubble), H_2O_2 (30%) and TBHP (70%) were used to replace oxygen (balloon).

2.5 Comparative kinetic study of the oxidation of 2,6-dimethylphenol with Co(II)-salen catalyst

The general oxidation procedure utilizing Co(II)-salen as catalyst was carried out, at different reaction times proceeded: 1, 2, 3, 5, 7, 10, 16 and 24 hr. An aliquot (1 mL) of the reaction mixture was taken, worked up and analyzed by GC.

2.6 Oxidation of other phenols

Selected phenols, namely phenol, 2-chlorophenol, 2,6-dimethoxyphenol, 2,6-di-*tert*-butylphenol, 2,3-dimethylphenol, 2,5-dimethylphenol, hydroquinone, 2-chlohydroquinone, 2,3-dimethylhydroquinone, 2-methylhydroquinone, α-naphthol, β-naphthol, 2-*tert*-butylhydroquinone, 2,6-dimethylaniline, 2,6-di-*tert*-butyl-4-bromophenol, 2,4,6-tribromo-3-methylphenol and anthracene were used for the study on the selectivity of this developed oxidation reaction under the optimum conditions.

General isolation procedure

After the reaction was completed (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 dichloromethane or a mixture of hexane-dichloromethane or chloroform-ethyl acetate as an eluent. The equivalent fractions observed by TLC were combined and the solvents were completely evaporated. The residue was recrystallized by an appropriate solvent to yield the desired quinone.

2,6-Dimethylbenzoquinone: 83% yield, m.p. 68-70 ^{o}C (lit.[40] 68-71 ^{o}C), R_f 0.55 (CH_2Cl_2). IR (KBr): 2969, 1649 and 1607 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.06 (6H, s) and 6.52 (2H, s).

2,6-Dimethoxybenzoquinone: 83% yield, m.p. 240-250 ^{o}C (lit.[40] 256 ^{o}C), R_f 0.45 (CH_2Cl_2). IR(KBr): 3062, 1701 and 1645 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 3.50 (6H, s) and 5.71 (2H, s).

2,6-Di-tert-butylbenzoquinone: 97% yield, m.p. 65-66 ^{o}C (lit.[40] 65-67 ^{o}C), R_f 0.30 (CH_2Cl_2). IR(KBr): 2959 and 1602 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.30 (18H, s) and 6.50 (2H, s).

2,3-Dimethylbenzoquinone: 73% yield (from the oxidation of 2,3-dimethylphenol) and 91.00% yield (from the oxidation of 2,3-dimethylhydroquinone), m.p. 68-71 ^{o}C (lit.[40] 69-70 ^{o}C), R_f 0.50 (CH_2Cl_2). IR(KBr): 2921, 1659 and 1598 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.00 (6H, s) and 6.69 (2H, s).

2,5-Dimethylbenzoquinone: 87% yield, m.p. 70-73 ^{o}C (lit.[40] 69-72 ^{o}C), R_f 0.60 (CH_2Cl_2). IR(KBr) 2925, 1668 and 1605 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.04 (6H, s) and 6.57 (2H, s).

Benzoquinone: 33% yield, m.p. 108-110 ^{o}C (lit.[1] 115 ^{o}C), R_f 0.60 (CH_2Cl_2). IR (KBr): 1675 and 1590 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.79 (4H, s).

2-Methylbenzoquinone: 39% yield, m.p. 65-68 ^{o}C (lit.[40] 69 ^{o}C), R_f 0.70 (CH_2Cl_2). IR(KBr) 3050, 1650 and 1603 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 2.05 (3H, s) and 6.60-6.81 (3H, m).

2-tert-Butylbenzoquinone: 98% yield, m.p. 54-55 ^{o}C, R_f 0.76 (CH_2Cl_2). IR (KBr): 1660 and 1593 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 1.29 (9H, s) and 6.55-6.69 (3H, m).

1,4-Naphthoquinone: 60% yield, m.p. 123-127 ^{o}C (lit.[1] 124-125 ^{o}C), R_f 0.47 (chloroform-ethyl acetate (9:1)). IR (KBr): 2920 and 1665 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.00 (2H, s) and 7.60-8.30 (4H, m).

1,2-Naphthoquinone: 59% yield (from the oxidation of α-naphthol) and 9.67% yield (from the oxidation of β-naphthol), m.p. 140-144 ^{o}C (lit.[1] 145-147 ^{o}C, melts with decomposition), R_f 0.36 (chloroform-ethyl acetate (9:1)). IR(KBr): 2925 and 1663 cm^{-1}; ^{13}C-NMR (DMSO) δ (ppm): 127.2 (1C), 128.9 (2C), 130.8 (1C), 132.1 (1C), 134.1 (1C), 134.8 (1C), 150.1 (1C), 184.6 (1C) and 188.6 (1C).

2.7 Competitive studies of the oxidation of 2,6-dimethylphenol, 2,6-di-*tert*-butylphenol, 2,3-dimethylphenol and 2,3-dimethylhydroquinone

Following the general oxidation procedure, equimolar amount (1 mmol) of 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol; 2,3-dimethylphenol and 2,3-dimethylhydroquinone were used as competitive substrates in the reaction. Competition between the oxidation of 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol or that between the oxidation of 2,6-dimethylphenol and 2,3-dimethylphenol or that between the oxidation of 2,6-dimethylphenol and 2,3-dimethylhydroquinone were compared.

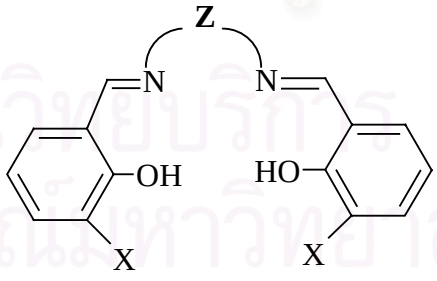
CHAPTER III

RESULTS AND DISCUSSION

The main features of this research focussed on the oxidation of phenols to quinones. The reaction conditions were optimized using 2,6-dimethylphenol as a chemical model substrate. Other substrates such as phenol, 2,6-dimethoxyphenol, 2,6-di-*tert*-butylphenol, 2,3-dimethylphenol, 2,5-dimethylphenol, hydroquinone, 2,3-dimethylhydroquinone, 2-methylhydroquinone, 2-*tert*-butylhydroquinone, α-naphthol, β-naphthol and anthracene were selected for examining the capability of catalyst and for exploring the scope of this developed oxidation system. Transition metal Schiff base complexes mainly Co(II)-salen were chosen as suited catalysts for this oxidation reaction.

3.1 Syntheses and characterization of Schiff base ligands and their complexes

Fourteen Schiff base ligands as shown below were synthesized by condensation reaction between selected aromatic aldehydes or ketones with primary diamines according to the literature procedure.[30-35]



a X = H, Z = -CH_2CH_2-

b X = H, Z = -$CH_2CH_2CH_2$-

c X = H, Z = -(*o*-C_6H_{10})-

d X = H, Z = -(*o*-C_6H_4)-

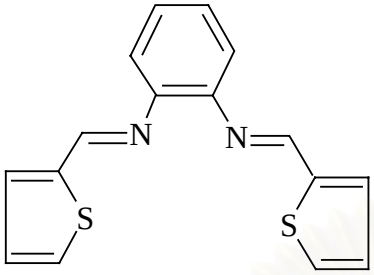
e X = H, Z = -(*m*-C_6H_4)-

f X = H, Z = -(*o*-C_6H_3-4-NO_2)-

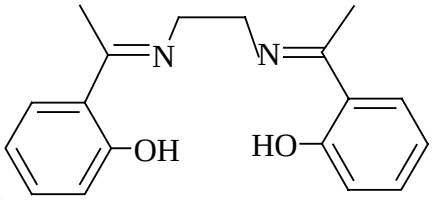
g X = H, Z = -(2,6-C_5H_3N)-

h X = OMe, Z = -CH_2CH_2-

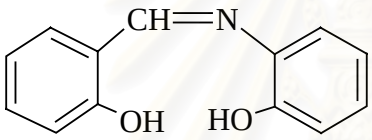
i X = OMe, Z = -(*o*-C_6H_4)-



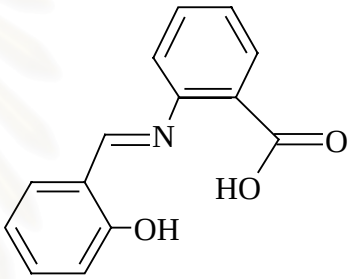
(j)



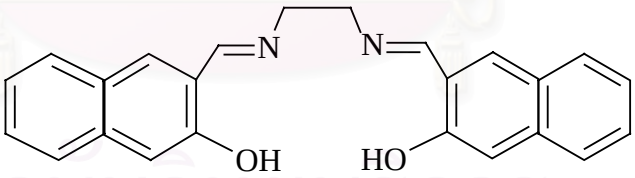
(k)



(l)



(m)



(n)

Their identities were well elucidated by TLC, IR and NMR techniques prior to use for synthesizing transition metal Schiff base complexes.[34] IR spectra of these complexes showed a characteristic absorption band in the range of 1600-1650 cm^{-1} attributable to an azomethine group (C=N) vibration. For free ligands, this band occurred at higher frequencies ~10-20 cm^{-1} which was belonged to C=N.[39]

3.2 Study on the optimum conditions for the oxidation of 2,6-dimethylphenol

Various factors were evaluated to optimize conditions of this oxidation reaction. 2,6-Dimethylphenol was selected as the first substrate as a chemical model. The variable parameters studied are effects of metal salen, cobalt complexes, cobalt (II) Schiff base complexes, type of solvents, amount of solvent, amount of catalyst, temperature and oxidants.

3.2.1 Effect of metal salen complexes

To search for the appropriate metal complexes that could catalyze the oxidation reaction of 2,6-dimethylphenol to 2,6-dimethylbenzoquinone in high yield, various metal salen complexes were screened. Table 3.1 presents the results of the utilization of various metal salen complexes on the oxidation of 2,6-dimethylphenol.

Table 3.1 The oxidation of 2,6-dimethylphenol catalyzed by various metal salen catalysts

Entry	Metal salen	2,6-dimethylbenzoquinone (%)
1	Cr(III)-salen.Cl	0
2	Cr(III)-salen.NO_3	0
3	Co(II)-salen	83
4	Fe(II)-salen	0
5	Cu(II)-salen	0
6	Mn(II)-salen	0
7	Ni(II)-salen	0
8	VO(II)-salen	0

reaction conditions : 2,6-dimethylphenol (1 mmol), metal salen (0.1 mmol), DMF (10 mL), 1 atm O_2 at room temperature for 24 hr

It is clearly seen from Table 3.1 that among eight transition metal salen complexes, only Co(II)-salen provided the yield of 2,6-dimethylbenzoquinone (entry 3). Thus, in this research the use of Co(II)-salen complex as a catalyst for oxidation of phenols will be focused.

3.2.2 Effect of cobalt complexes

The variation of cobalt salts and complexes was examined in order to observe the efficiency of each cobalt catalyst on the oxidation of phenols. The results are collected as shown in Table 3.2.

Table 3.2 The oxidation of 2,6-dimethylphenol catalyzed by cobalt salts and complexes

Entry	Cobalt complex	2,6-dimethylbenzoquinone (%)
1	Co(II)-salen	83
2	Co(II)-$(acetate)_2.4H_2O$	0
3	Co(II)-$Cl_2.6H_2O$	0
4	Co(II)-$(acac)_2.4H_2O$	0
5	Co(II)-$(stearate)_2$	0
4	Co(II)-$(palmitate)_2$	0

reaction conditions : 2,6-dimethylphenol (1 mmol), cobalt complex (0.1 mmol), DMF (10 mL), 1 atm O_2 at room temperature for 24 hr

As it is clearly seen from Table 3.2 that no other cobalt complexes could be used as a catalyst for the oxidation of 2,6-dimethylphenol as Co(II)-salen complex. This is possibly due to the capability of Co(II)-salen to bind with O_2 to make an efficient complex as that reported in literature.[25-26] Other cobalt Schiff base complexes were then synthesized and screened for their catalytic oxidation of this phenol as discussed in the following topic.

3.2.3 Effect of Co(II)-Schiff base complexes on the oxidation of 2,6-dimethylphenol

The effect of Co(II)-Schiff base catalyst on the reactivity of 2,6-dimethylphenol oxidation was studied. In the presence of Schiff base ligands, *i.e*. salen **(a)**, saltn **(b)**, salcycloen **(c)**, sal-*o*-phene **(d)**, sal-*m*-phene **(e)**, sal-(4-nitro)-*o*-phene **(f)**, sal-py-2,6-diimine **(g)**, salen-OMe **(h)**, 3-OMesalophene **(i)**, thiophen-*o*-phen **(j)**, Mesalen **(k)**, salop **(l)**, saloa **(m)**, *Bis*(nap) **(n)** and pyr(Co-salen) coordinating with cobalt(II), the effects of various cobalt-Schiff base catalysts on the oxidation of 2,6-dimethylphenol are summarized in Table 3.3 and Figure 3.1.

Table 3.3 The effect of various cobalt-Schiff base complexes for the oxidation of 2,6-dimethylphenol

Entry	Schiff base ligands	2,6-dimethylbenzoquinone (%)
1	Salen	83
2	Saltn	0
3	Salcycloen	72
4	sal-*o*-phene	12
5	sal-*m*-phene	0
6	sal-(4-nitro)-*o*-phene	0
7	sal-py-2,6-diimine	0
8	salen-OMe	57
9	3-OMesalophene	61
10	thiophen-*o*-phen	0
11	Mesalen	64
12	Salop	4
13	Saloa	0
14	*Bis*(nap)	62
15	pyr(Co-salen)	0

reaction conditions : 2,6-dimethylphenol (1 mmol), cobalt(II)-Schiff base complex (0.1 mmol), DMF (10 mL), 1 atm O_2 at room temperature for 24 hr

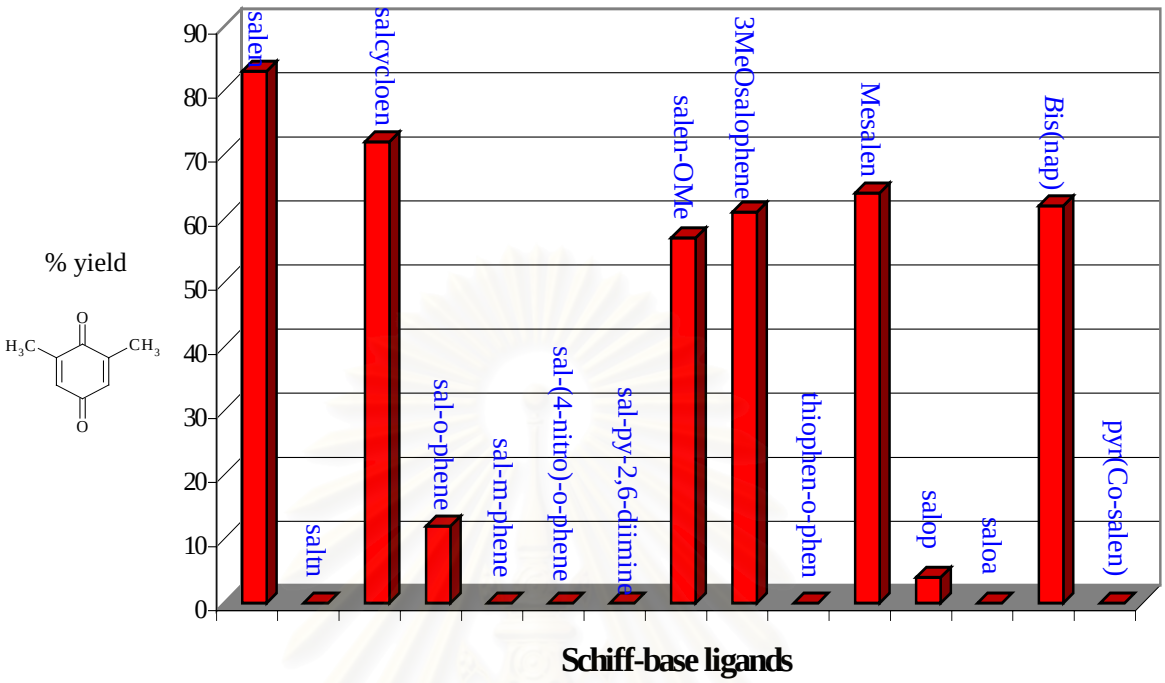
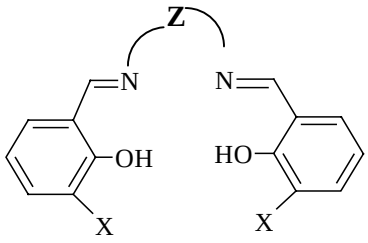


Figure 3.1 The effect of various cobalt Schiff base complexes for the oxidation of 2,6-dimethylphenol

As seen from Table 3.3 and Figure 3.1, it could be verified that the oxidation was influenced by the structure of Co(II)-Schiff base catalysts. It is interesting to note that cobalt catalysts with Schiff base ligands in entries 1, 3, 8, 9, 11 and 14 gave better results than the systems employing other Schiff base ligands studied. It could also be observed that the conversion of 2,6-dimethylphenol to 2,6-dimethylbenzoquinone with O_2/Co(II)-Schiff base system, that occurred *via* superoxo Co/O_2 intermediate was dependent on the size of nucleating ligands and the substituent of a Schiff base ligand.



Considering the variation of diimine linkage, **(Z)** on Schiff base ligands, $-CH_2CH_2-$, -(*o*-C_6H_{10})- and -(*o*-C_6H_4)- possessed a compact structure which was not of long chain between these two nitrogen atoms seemed to be a good ligand. This observation could be endorsed by the yields of the desired products utilized these catalysts. Other catalysts possessing a longer chain between nitrogen atoms, Z = $-CH_2CH_2CH_2-$ and -(*m*-C_6H_4)-, were catalytically inactive. From this experiment, Co(II)-salen (Z = $-CH_2CH_2-$, X = H) provided the highest yield, perhaps because no steric effect on Schiff base ligand rendered its catalytic activity.

3.2.4 Effect of the amount of Co(II)-salen for the oxidation of 2,6-dimethylphenol

The effect of the amount of Co(II)-salen for the oxidation of 2,6-dimethylphenol was studied by varying the amount of Co(II)-salen catalyst, *i.e.* 0, 0.02, 0.05, 0.10, 0.15, 0.20 and 0.30 mmol. The results are shown in Table 3.4 and Figure 3.2.

Table 3.4 The effect of the amount of Co(II)-salen for the oxidation of 2,6-dimethylphenol

Entry	Co-salen (mmol)	2,6-dimethylbenzoquinone (%)	turnover
1	0	0	-
2	0.02	27	17
3	0.05	67	16
4	0.10	83	10
5	0.15	67	5
6	0.20	73	5
7	0.30	57	2

reaction conditions : 2,6-dimethylphenol (1 mmol), DMF (10 mL), 1 atm O_2 and reaction time at room temperature for 24 hr

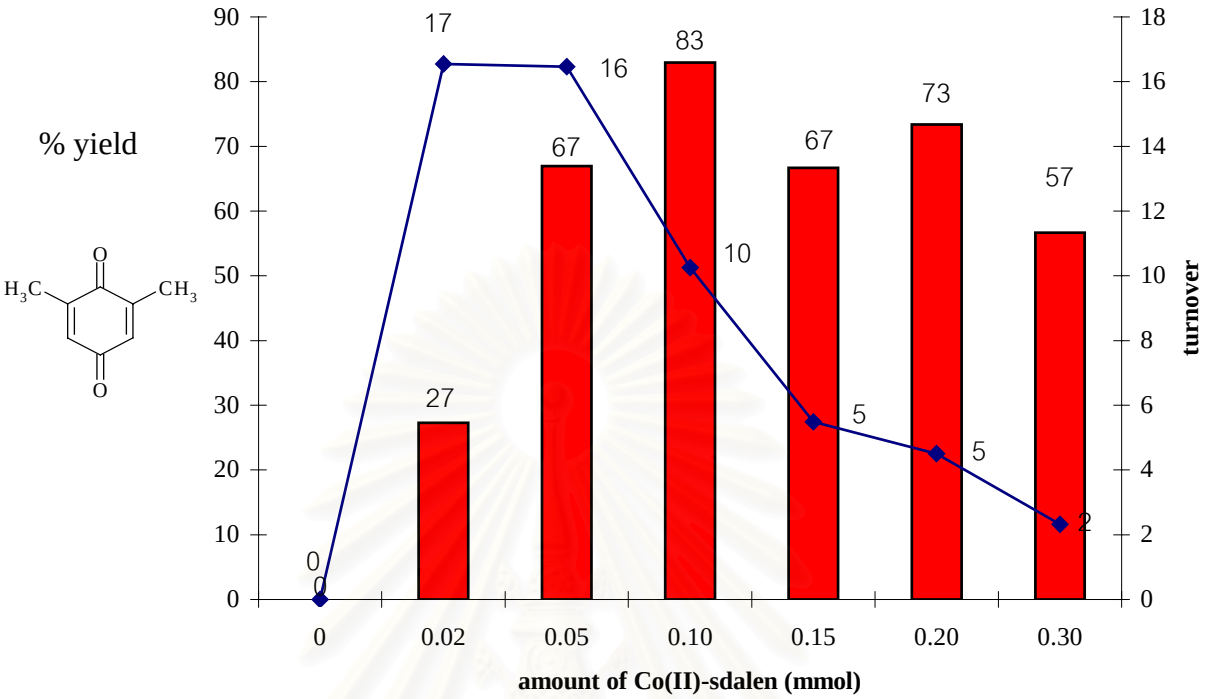


Figure 3.2 Effect of the amount of Co(II)-salen for the oxidation of 2,6-dimethylphenol

From Table 3.4 and Figure 3.2, no reaction took place without Co(II)-salen catalyst (entry 1). When 0.10 mmol of Co(II)-salen was utilized, the reaction gave almost quantitative yield of desired product (entry 4). Nonetheless, employing more catalyst (entries 5-7) the yield of desired products decreased. This was perhaps stemmed from the reaction media contained insoluble Co(II)-salen catalyst. The turnover number was depended on the amount of catalyst used. The highest number was 17.

3.2.5 Kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

The kinetic study of the reaction was performed in order to find the optimum time for the progress of the reaction. However, the rate of these reactions was generally slow and needed more time to complete. The rate of 2,6-dimethylphenol oxidation catalyzed by Co(II)-salen complex using oxygen (O_2) as oxidant in DMF was examined. The kinetic analysis results are shown in Table 3.5 and Figure 3.3.

Table 3.5 Kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

Entry	Time (hr)	2,6-dimethylbenzoquinone (%)
1	1	34
2	3	65
3	5	83
4	7	81
5	10	78
6	16	80
7	24	81

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2 at room temperature

From Figure 3.3, in the variation of times; 1, 3, 5, 7, 10, 16 and 24 hr, it was found that the reaction time of 5 hr was the most appropriate time for the oxidation of 2,6-dimethylphenol under this particular system.

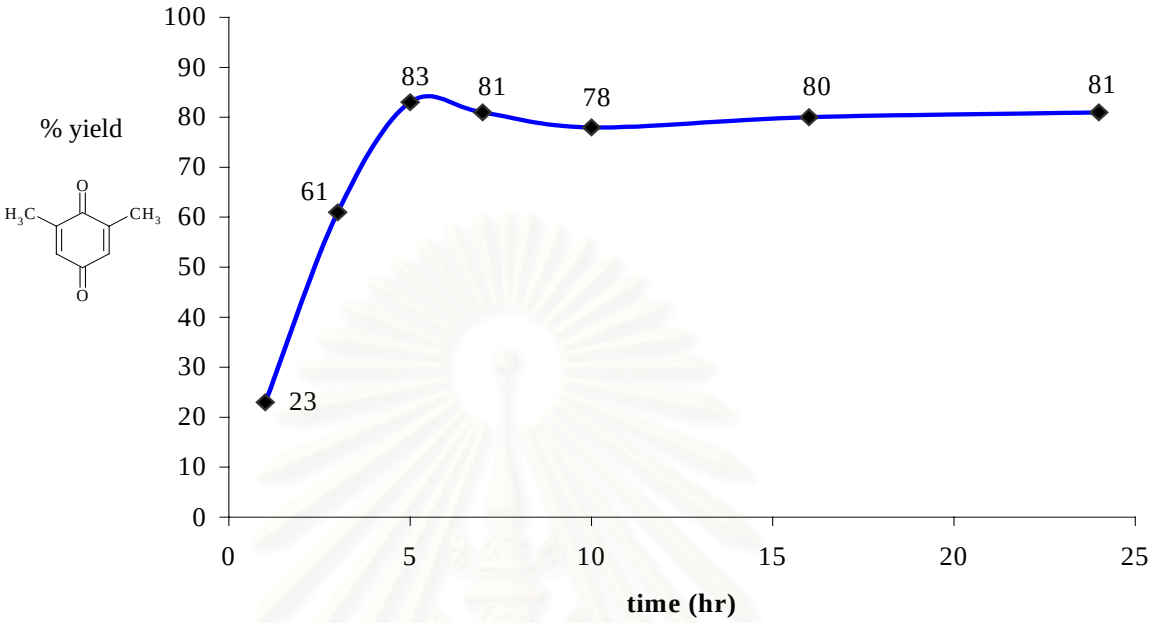


Figure 3.3 Kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

3.2.6 Effect of solvent on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen complex

In this study, the solvent that could provide a homogeneous reaction was required. From the experiment described above, DMF was the first solvent chosen as a reaction media because it could dissolve both cobalt Schiff base catalysts and substrate. Other solvents such as ethanol, acetonitrile, acetone, methanol, 1,2-dichloroethane, THF, dichloromethane, chloroform, pyridine and carbon tetrachloride were chosen to examine whether they can replace DMF in this oxidation reaction. The results are shown in Table 3.6 and Figure 3.4.

Table 3.6 The effect of solvent on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)- salen

Entry	Solvent	2,6-dimethylbenzoquinone (%)
1	DMF	83
2	Ethanol	5
3	Acetonitrile	49
4	Acetone	7
5	Methanol	6
6	1,2-Dichloroethane	8
7	THF	21
8	Dichloromethane	9
9	Chloroform	0
10	Pyridine	0
11	Carbon tetrachloride	0

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), solvent (10 mL), 1 atm O_2 at room temperature for 5 hr

From Table 3.6 and Figure 3.4, it was found that when acetonitrile and THF were used as solvent, the oxidation reaction could proceed and provided higher amount of product than in the case of employing other solvents, except for DMF. This may be accounted that unwanted side reactions may rapidly occur instead. In general, stronger hydrogen bonding solvents such as ethanol and methanol slow the rate of the reaction.[28] When chloroform, carbon tetrachloride and pyridine were used as solvents, no reaction took place, because these solvents may trap the free radical intermediate present in the reaction. Therefore, an appropriate solvent for this particular reaction is DMF. The comparative kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen in DMF, acetonitrile and THF are discussed in the forthcoming section.

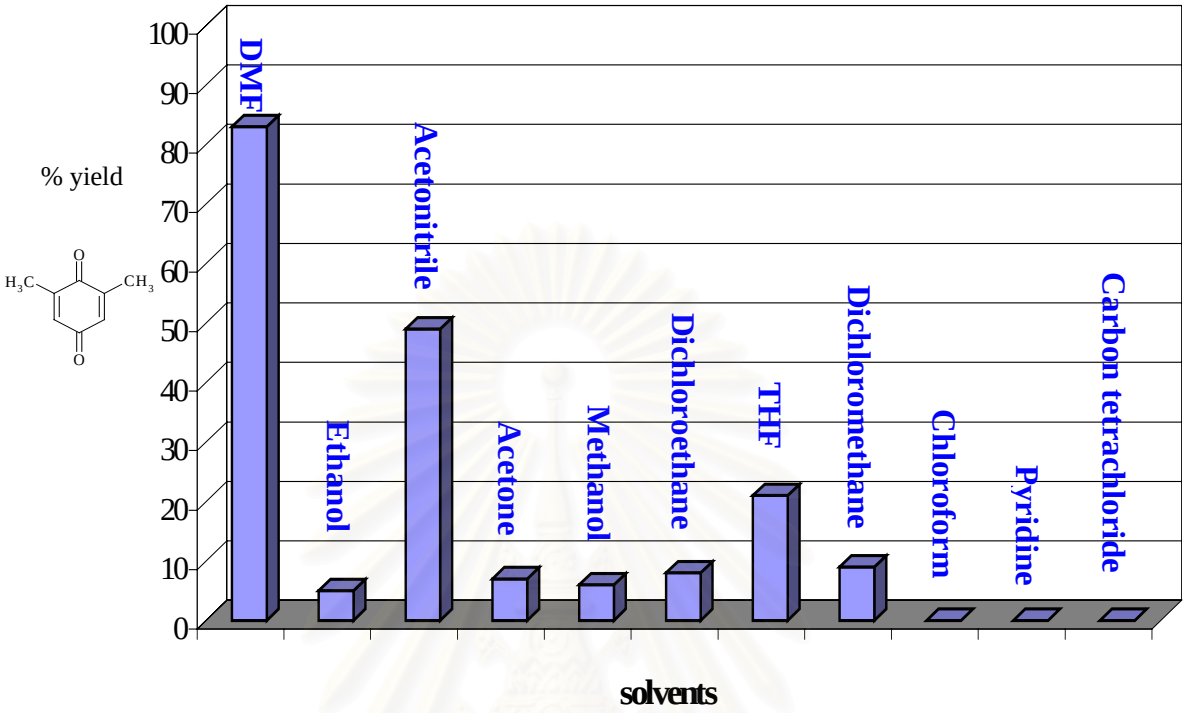


Figure 3.4 Effect of solvent on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)- salen

3.2.7 Comparative kinetic study on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen in DMF, THF and acetonitrile

The kinetic study on the reaction rate of the oxidation of 2,6-dimethylphenol by various solvents: DMF, THF and acetonitrile was conducted at room temperature. The results are shown in Table 3.7 and Figure 3.5.

As seen from Figure 3.5, it was found that the rate of the reaction depended greatly on type of solvents. The reaction in DMF could proceed smoothly faster than in acetonitrile and in THF, respectively. The half-lifes of the reaction were increased from approximately 2 hr in DMF to 3 hr in acetonitrile and 10 hr in THF. However, the final yield of product (for the reaction time 24 hr) in the presence of DMF, THF and acetonitrile as solvents were in the vicinity. Therefore, an appropriate solvent for this reaction was DMF. Moreover in the case of employing acetonitrile and THF, the catalyst was not soluble at room temperature. These solvents have indeed lower

boiling point than DMF which are perhaps easy to evaporate during the reaction took place.

Table 3.7 Comparative kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen in DMF, THF and acetonitrile

Entry	Time (hr)	2,6-dimethylbenzoquinone (%)		
		DMF	THF	Acetonitrile
1	1	23	0	7
2	3	61	11	40
3	5	83	14	58
4	7	81	18	75
5	10	78	35	76
6	16	80	71	78
7	24	81	76	76

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), solvent (10 mL), 1 atm O_2 at room temperature

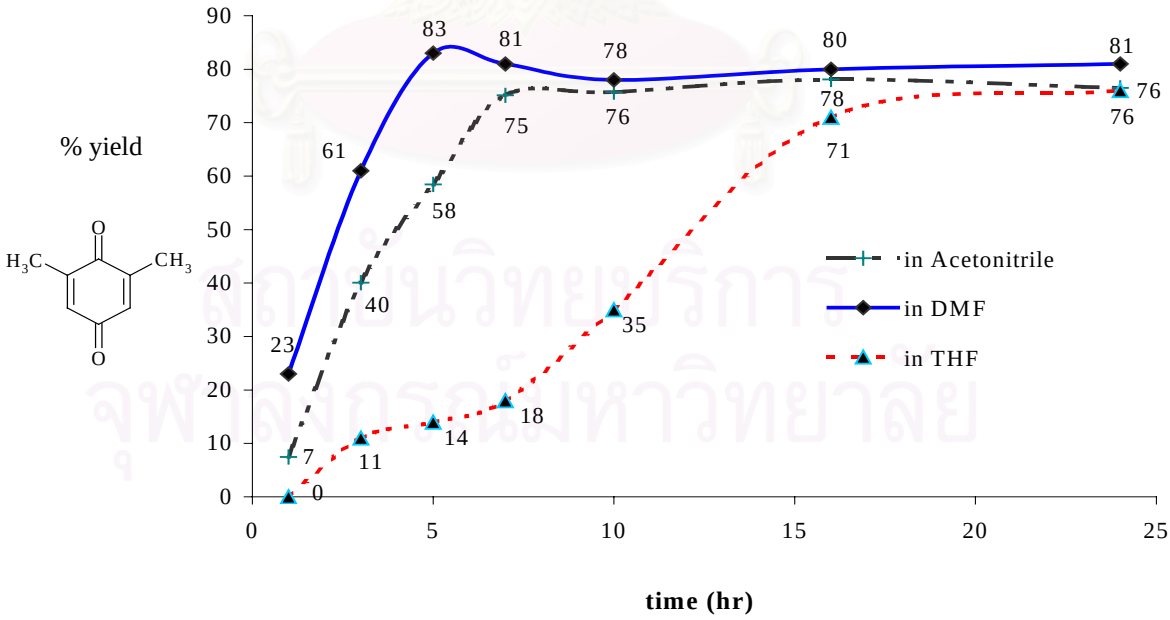


Figure 3.5 Comparative kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen in DMF, THF and acetonitrile

3.2.8 Effect of the amount of DMF on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

Another important feature that needs to be studied was the effects of the amount of solvent employed. DMF was selected as a solvent to examine. The results of the variation of the amount of DMF affected the oxidation of 2,6-dimethylphenol are collected in Table 3.8 and Figure 3.6.

Table 3.8 Effect of the amount of DMF for the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

Entry	amount of DMF (mL)	2,6-dimethylbenzoquinone (%)
1	3	87
2	5	91
3	10	83
4	15	58
5	20	18

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), 1 atm O_2 at room temperature for 5 hr

From Table 3.8 and Figure 3.6, it is interesting to note that when employing DMF 3 and 5 mL (entries 1-2) the desired product was produced a little bit higher than the former conditions employing DMF 10 mL. When the amount of DMF increased more than 10 mL (entries 4 –5), on the other hand the lower yield was detected. It could also be observed that the oxidation of 2,6-dimethylphenol in this system was dependent on the interaction of catalyst with oxidant and substrate. However, in the case of employing DMF 3 and 5 mL that even gave higher yield, the catalyst was found not to completely soluble in the reaction medium. Therefore, an appropriate amount of solvent for this reaction was 10 mL.

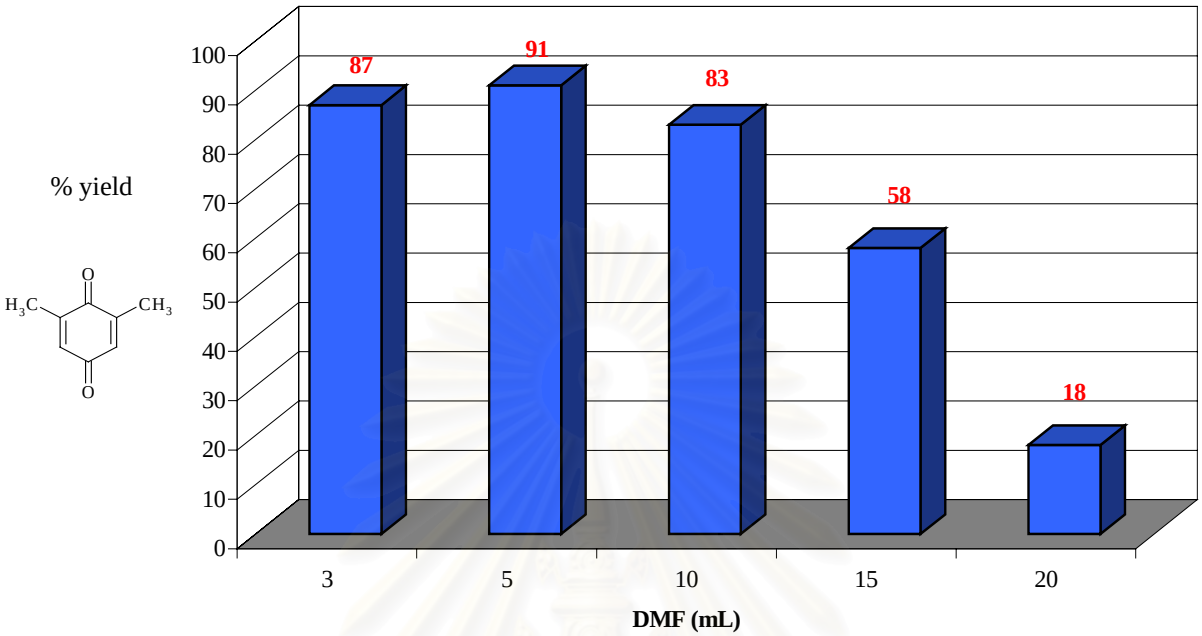


Figure 3.6 The effect of the amount of DMF for the oxidation of 2,6-dimethylphenol catalyzed by Co-salen (5 hr)

3.2.9 Effect of temperature on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

The oxidation of 2,6-dimethylphenol described above was carried out at room temperature. From Figure 3.3, the half-life of the reaction was approximately 2 hr. The rate of the oxidation reactions at 45 ^{o} and 60 ^{o}C was explored to compare the effect of temperature during time interval of 5 hr. The results are presented in Table 3.9.

Table 3.9 The effect of temperature on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

Entry	Temperature (^{o}C)	2,6-dimethylbenzoquinone (%)
1	≈ 28 (RT)	83
2	45	86
3	60	87

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2 for 5 hr

From the results attained, it could be observed that the reactions at higher temperature (entries 2-3) gave comparable yields of quinone to that performed at room temperature. Nevertheless, it is also interesting to observe the rate of this reaction at higher temperature.

The rate of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen at RT (28 ^{o}C), 45 ^{o}C and 60 ^{o}C was examined. The results are presented in Table 3.10 and Figure 3.7.

Table 3.10 Comparative kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen at RT, 45 ^{o}C and 60 ^{o}C

Entry	Time (min)	2,6-dimethylbenzoquinone (%)		
		at RT	at 45 ^{o}C	at 60 ^{o}C
1	10	5	18	33
2	20	7	44	58
3	30	10	64	72
4	40	14	77	79
5	50	19	82	83
6	60	23	83	88
7	120	41	85	85
8	180	61	87	86
9	300	83	86	87

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2

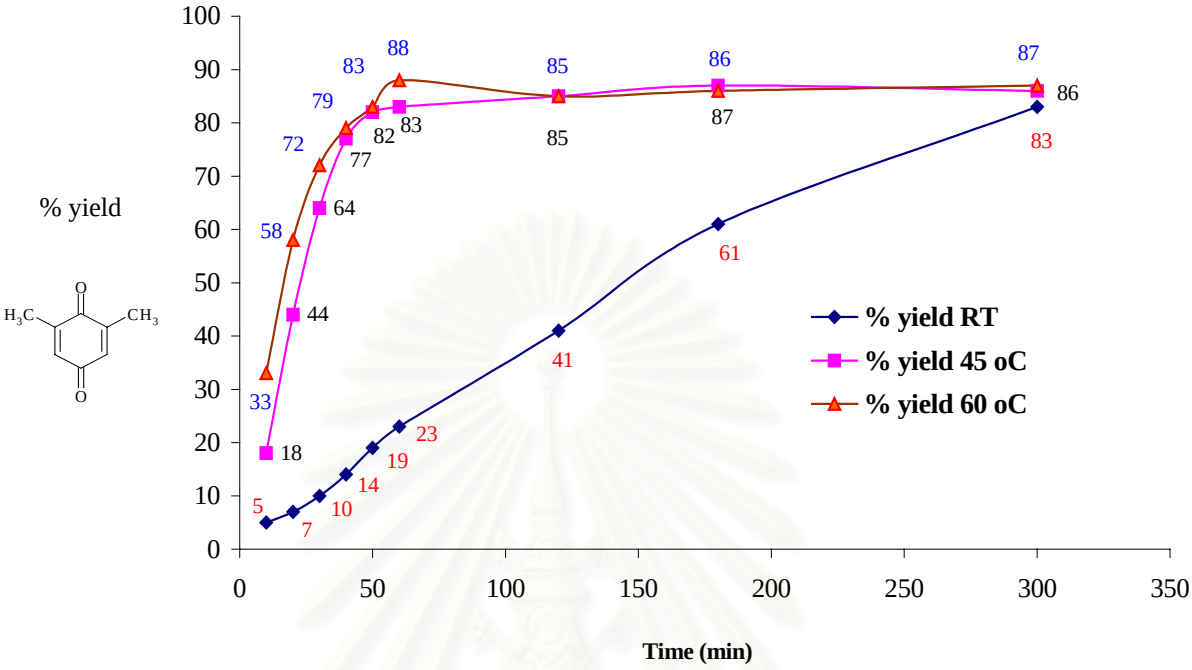


Figure 3.7 Comparative kinetic study on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen at RT, 45 ^{o}C and 60 ^{o}C

It could clearly be seen from this figure that the rate of the oxidation reaction of 2,6-dimethylphenol proceeded at high temperature quite faster than that at room temperature. The half-lifes of the reaction were deduced from approximately 2 hr at room temperature to 20 min at 40 ^{o}C and 15 min at 60 ^{o}C with almost the same amount of quinones obtained.

3.2.10 Effect of oxidants on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

Oxygen (O_2) was a primary oxidant used for the oxidation of 2,6-dimethylphenol in this study. Another question was then arose whether oxygen was an important oxidant used in the reaction or other oxidants could be used to replace oxygen. Air, H_2O_2 (30%) and TBHP (70%) were therefore selected for this verification, as summarized in Table 3.11.

Table 3.11 The effect of oxidant on the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen

Entry	Oxidant	2,6-dimethylbenzoquinone (%)
1	no oxidant	0
2	air	52
3	oxygen (balloon)	83
4	oxygen (bubble)	95
5	H_2O_2 (30%)	0
6	TBHP (70%) at RT	0
7	TBHP (70%) at 60 ^oC	trace

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL) at room temperature or specified for 5 hr

It was found that no reaction took place without the oxidant (entry 1), and the oxidation of 2,6-dimethylphenol could be generally oxidized in the presence of oxygen. The oxygen from air (entry 2) gave lower yield of quinone than the pure oxygen in balloon or with O_2 bubble (to flow the bubble of O_2 pass into the reaction mixture until the reaction finished) (entries 3-4). However, when H_2O_2 (30%) and TBHP (70%) were used as oxidants (entries 5-6), it was found that no reaction took place at room temperature or even at 60 ^oC with TBHP (70%) (entry 7).

It is worth summarizing at this point that upon reaction optimization examined, the optimum conditions for the oxidation of 2,6-dimethylphenol could be concluded as follows: 1 mmol of phenol as a substrate, 10 mL DMF as solvent, 0.1 mmol Co(II)-salen complex as catalyst, O_2 (balloon) as oxidant and reaction time of 5 hr at room temperature.

Under this particular condition, 2,6-dimethylphenol could be transformed into 2,6-dimethylbenzoquinone in high yield (83% GC-yield, 80% isolated yield) with 100% conversion. The attempt to isolate the quinone product by column chromatography was accomplished. The isolation procedure was described in Chapter II. The product quinone as yellow needle 80% was attained, m.p. 68-70 ^oC (lit.[40] 68-71 ^oC), R_f 0.55 (CH_2Cl_2). IR(KBr): 2969 (C-H stretching vibration), 1649 (C=O stretching vibration of diketone) and 1607 (C=C stretching) cm^{-1}; ^{1}H-NMR

($CDCl_3$) δ (ppm): 2.06 (methyl protons, 6H, s) and 6.52 (alkenic protons, 2H, s). The IR and NMR spectra are shown in Figures 3.8 and 3.9.

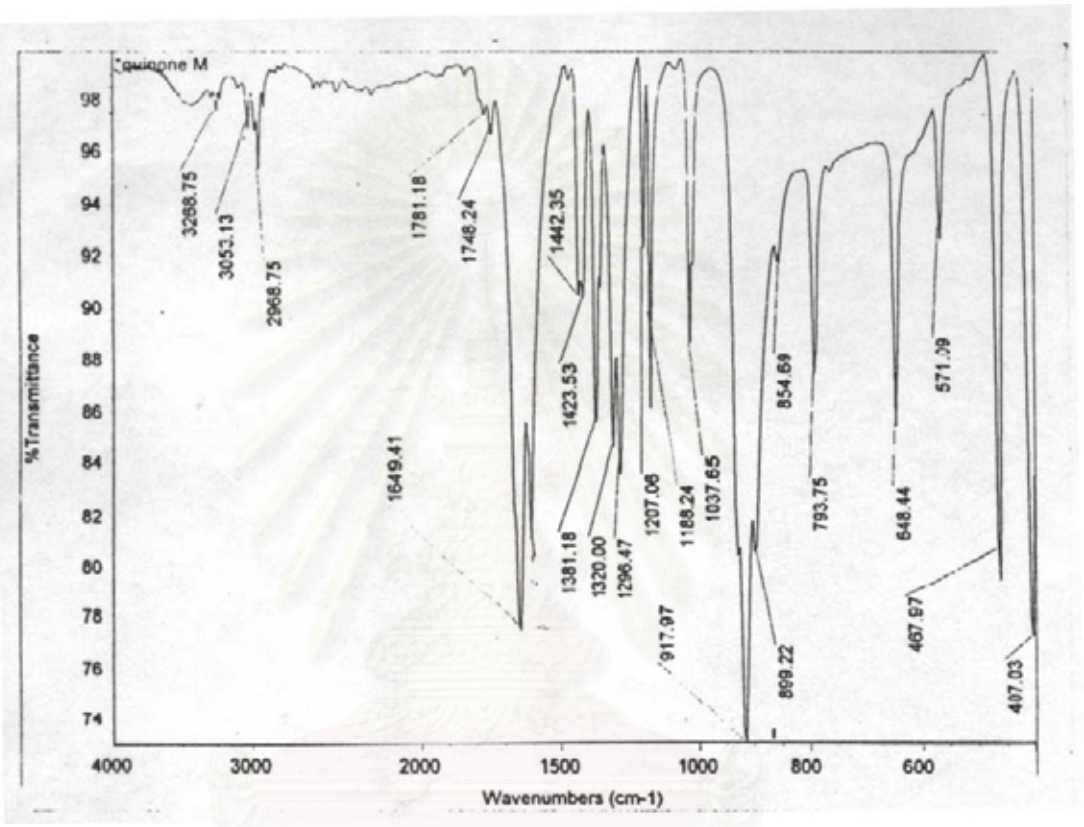


Figure 3.8 IR spectrum of isolated 2,6-dimethylbenzoquinone

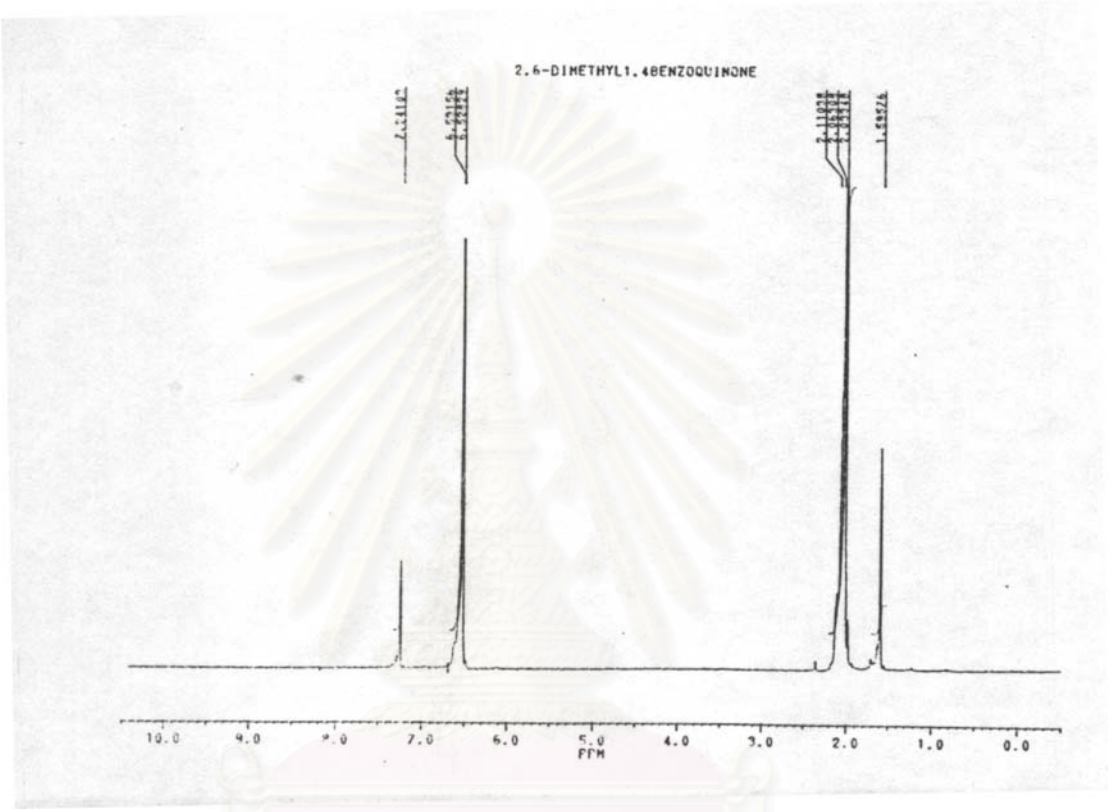
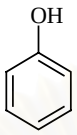
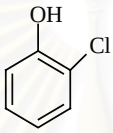
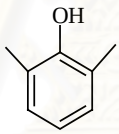
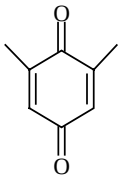
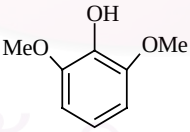
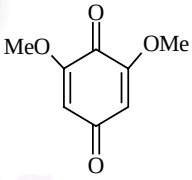


Figure 3.9 ^{1}H-NMR spectrum of isolated 2,6-dimethylbenzoquinone

3.3 Oxidation of other phenols catalyzed by Co(II)-salen complex

To extend the scope of the oxidation of phenols catalyzed by Co(II)-salen complex, various phenols and related compounds were selected. These include phenol, *o*-cresol, 2,6-dimethoxyphenol, 2,6-di-*tert*-butylphenol, 2,3-dimethylphenol, 2,5-dimethylphenol, hydroquinone, 2,3-dimethylhydroquinone, 2-methylhydroquinone, α-naphthol, β-naphthol, 2-*tert*-butylhydroquinone, 2,6-dimethylaniline, 2,6-di*tert*-butyl-4-bromophenol, 2,4,6-tribromo-3-methylphenol and anthracene. The results are presented in Table 3.12.

Table 3.12 Oxidation of other phenols catalyzed by Co(II)-salen[a]

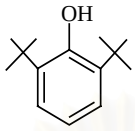
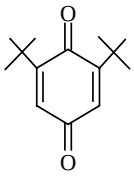
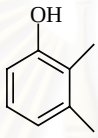
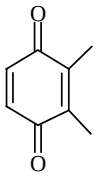
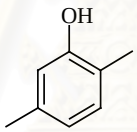
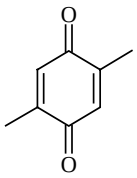
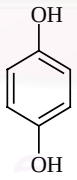
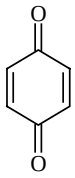
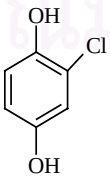
Entry	Substrate	Product (s) (%)
1		no reaction
2		no reaction
3		 80[b] 83[c]
4		 83[b] (30 min)

a. **reaction conditions** : phenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2 and at room temperature for 5 hr

b. Isolated yield

c. yield determined by gas chromatography (GC)

Table 3.12 (cont)

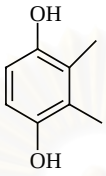
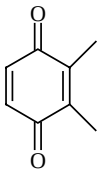
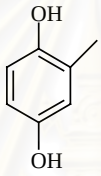
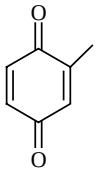
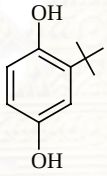
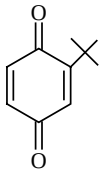
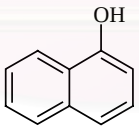
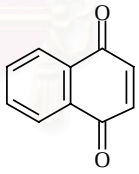
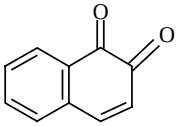
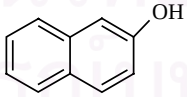
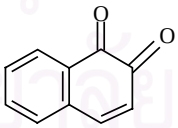
Entry	Substrate	Product (s) (%)
5		 95[b] 97[c]
6		 70[b] 73[c]
7		 80[b] 87[c]
8		 33[b]
9		no reaction

a. **reaction conditions** : phenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2 and at room temperature for 5 hr

b. Isolated yield

c. yield determined by gas chromatography (GC)

Table 3.12 (cont)

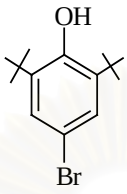
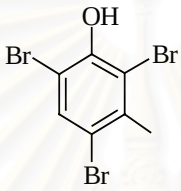
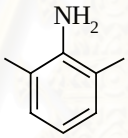
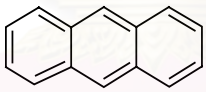
Entry	Substrate	Product (s) (%)
10		 63[b] 91[c]
11		 39[b]
12		 82[b] 98[c]
13		  59[b] 60[c] 10[b]
14		 59[b]

a. **reaction conditions** : phenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2 and at room temperature for 5 hr

b. Isolated yield

c. yield determined by gas chromatography (GC)

Table 3.12 (cont)

Entry	Substrate	Product (s) (%)
15		no reaction
16		no reaction
17		no reaction
18		no reaction

a. **reaction conditions** : phenol (1 mmol), Co(II)-salen complex (0.1 mmol), DMF (10 mL), 1 atm O_2 and at room temperature for 5 hr

From the results obtained, it was clearly exhibited that all phenols and hydroquinones that used as substrates could be converted to their analogous quinones as predominant products in high yield, except for phenol, 2-chlorophenol, 2-chlorohydroquinone, 2,6-di*tert*-butyl-4-bromophenol, 2,4,6-tribromo-3-methylphenol 2,6-dimethylaniline and anthracene (entries 1-2, 9 and 15-18). It could also observe that the oxidation of phenols to their quinones depended on the substituents on the benzene ring of phenols. With unsubstituted phenols (entry 1), no reaction took place. This was not perhaps of rich electrons density on the benzene ring

that could be influenced to stabilize the O-H bond on a hydroxyl group. Thus H atom on the hydroxyl group was a poor leaving group. Further supporting evidence for this prior result was when using electron-withdrawing chloride and bromide group as substitutent (entries 2, 9, 15 and 16), no reaction took place .

The oxidation of 2,6-di-*tert*-butylphenol (entry 5) gave higher yield than 2,6-dimethylphenol (entry 3). This may be explained that *tert*-butyl groups were better electron donor than methyl group. Therefore the oxidation reaction could easily take place. The rich electron density on the benzene ring decreased the stabilization of the O-H bond on hydroxyl group. Consequently, the hydrogen atom on the hydroxyl group became a good leaving group. However, the oxidation of dimethyl substituted phenols could also be converted in high yield to the corresponding quinone (entries 3, 6 and 7). This result could be strongly indicated that there was nearly no effect of the position of dimethyl substitution involved in this oxidation reaction. In addition, the oxidation of 2,6-dimethoxyphenol (entry 4) gave high yield and the rate of reaction was quite fast. The quinone product was precipitated out after the 30 min.

In the case of hydroquinones, the results were almost the same as those for phenols. The yields of the corresponding products were increased when electron-donating groups as substituents were present (entries 8, 10, 11 and 12). It was also observed that the oxidation of hydroquinones gave higher yield than phenols when the same substituents were compared (entries 6 and 10).

The oxidation of α-naphthol and β-naphthol was studied under the same conditions. The results are shown in Table 3.12 (entries 13 and 14). It was found that in the case of α-naphthol, 1,4-naphthoquinone was detected as a major product and 1,2-naphthoquinone being a minor. On the other hand, β-naphthol, after the reaction was over within 5 hr, the whole reaction mixture was extracted and separated by silica gel column chromatography eluting with chloroform-ethyl acetate (9:1) to furnish 59 % yield of 1,2-naphthoquinone as the sole product.

No reaction was observed with anthracene as substrate. This result implied that anthracene C-H bond is stable under this particular condition, that difficult to be oxidized to quinone product. For the oxidation of 2,6-dimethylaniline, no reaction to quinone took place. This result implied that the stable C-N bond was difficult to be oxidized to C=O under this condition. Other substrates such as *o*-cresol,

o-vanillin, 1,4-dihydroxyanthraquinone, 1,5-dihydroxyanthraquinone and 1,8-dihydroxyanthraquinone were also tested; however, no reaction took place under this studied conditions.

3.4 The oxidation of 2,6-dimethylphenol using TBHP as oxidant

The oxidation of 2,6-dimethylphenol with TBHP as oxidant was also investigated in this research. From the experimental described above, nearly no reaction took place with TBHP as oxidant when employing DMF as solvent at both room temperature and 60 ^{o}C. Other solvents were chosen to examine whether they can alter the oxidation reaction with TBHP. The results are presented in Table 3.13 and Figure 3.7.

Table 3.13 Variation of solvent in the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen complex with TBHP as oxidant

Entry	Solvent	% yield	
		5 hr	24 hr
1	DMF	trace	trace
2	Acetonitrile	7	4
3	Methanol	2	4
4	Dichloromethane	21	32
5	Chloroform	39	50
6	Carbon tetrachloride	11	24
7	Benzene (60 ^{o}C)	37	39
8	THF	trace	trace

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), solvent (10 mL), TBHP (70%) (9 mmol) at room temperature

From Table 3.13 and Figure 3.7, when acetonitrile, methanol, dichloromethane, chloroform, carbon tetrachloride and THF were used to replace DMF in the oxidation reaction with TBHP, nearly all of these solvents allowed the oxidation to take place, except THF. Employing chloroform (entry 5) the oxidation could produce higher

yield of quinones than other solvents. The rate of the reaction was observed to be faster than those in other reaction media. Therefore, an appropriate solvent for this reaction was chloroform. The optimum condition for using TBHP as oxidant will be explored in the following topic.

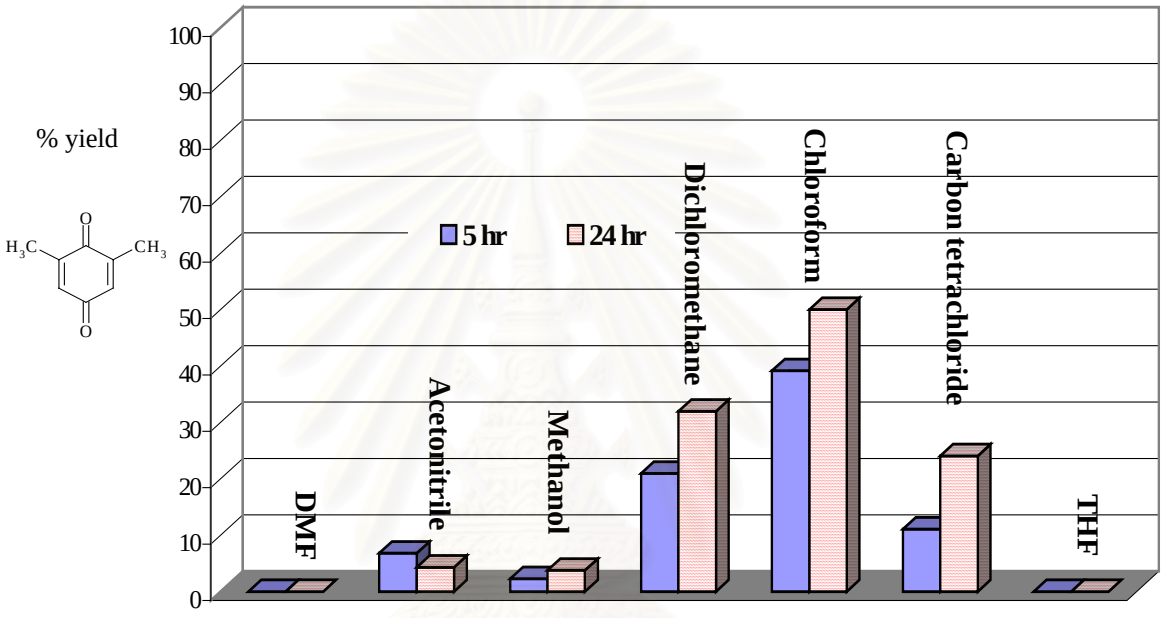


Figure 3.10 Variation of solvent in the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen complex with TBHP as oxidant

3.4.1 Study on the optimum conditions for the oxidation of 2,6-dimethylphenol with TBHP as oxidant

The variation of the amount of TBHP for the oxidation of 2,6-dimethylphenol was examined at room temperature and at 60 ^{o}C to find the optimum conditions. The results are shown in Table 3.14.

Table 3.14 Variation of the amount of TBHP in the oxidation of 2,6-dimethylphenol at RT and 60 ^{o}C

Entry	Temp. (^{o}C)	TBHP(mmol)	%yield	
			5 hr	24 hr
1	RT	9	39 (5)*	50 (8)*
		18	13 (1)*	32 (2)*
2	60 ^{o}C	9	50 (8)*	43 (6)*
		18	7 (1)*	31 (2)*

reaction conditions : 2,6-dimethylphenol (1 mmol), Co(II)-salen complex (0.1 mmol), $CHCl_3$ (10 mL), * % yield based on TBHP

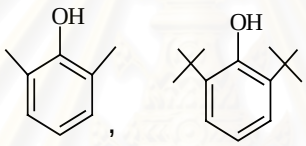
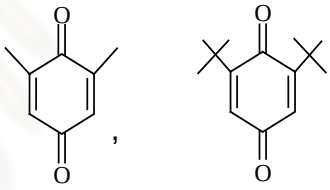
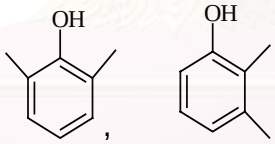
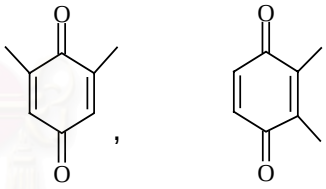
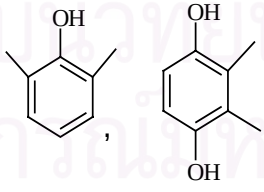
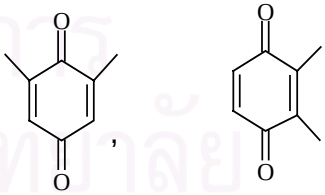
As seen from Table 3.14, it was found that when the amount of oxidant increased doubly, the desired product was dramatically decreased. This may be explained that unwanted side reactions may rapidly occur instead or the amount of TBHP and H_2O was excess for this reaction thence the steric hindrance may affect in solution. However, in the case of employing 9 mmol TBHP, the rate of the conversion of 2,6-dimethylphenol to the desired product was increased when the reaction temperature was increased (entry 2).

According to the experimental results, the optimum conditions for the oxidation of 2,6-dimethylphenol with TBHP as oxidant could be concluded as follows: 1 mmol of phenol as a substrate, 10 mL of chloroform as solvent, 0.1 mmol of Co(II)-salen as catalyst, 9 mmol of TBHP as an oxidant, reaction time of 5 hr and reaction temperature at 60 ^{o}C. The highest yield based on TBHP was 8% when employing 9 mmol of TBHP at 60 ^{O}C for 5 hr (entry 2).

3.5 Competitive study on the oxidation of 2,6-dimethylphenol, 2,6-di-*tert*-butylphenol, 2,3-dimethylphenol and 2,3-dimethylhydroquinone

In order to examine the characteristic of this developed catalytic system, the competitive studies on the oxidation between 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol, and 2,3-dimethylphenol and 2,3-dimethylhydroquinone were investigated. The results are presented in Table 3.15.

Table 3.15 Competitive study on the oxidation of 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol; 2,3-dimethylphenol and 2,3-dimethylhydroquinone

Entry	Substrate	Product (s) (%)
1		 79 96
2		 76 68
3		 73 89

reaction conditions : substrate (1 mmol each), Co(II)-salen complex (0.1 mmol), solvent (10 mL), 1 atm O_2 at room temperature for 3 hr

From Table 3.15, it was found that the better electron-donating substituents of 2,6-di-*tert*-butylphenol was, the faster the oxidation reaction observed (entry 1). The reason for this may be because the rich electron density on benzene ring decreased the stabilization of the O-H bond on the hydroxyl group. Therefore, the hydrogen atom on the hydroxyl group of 2,6-di-*tert*-butylphenol was a better leaving group than those of 2,6-dimethylphenol.

Entry 2 was designed to observe the rate of the oxidation of dimethyl substituted phenols to the corresponding quinone. It was detected that it was no significant effect when the substituted position of dimethyl was varied.

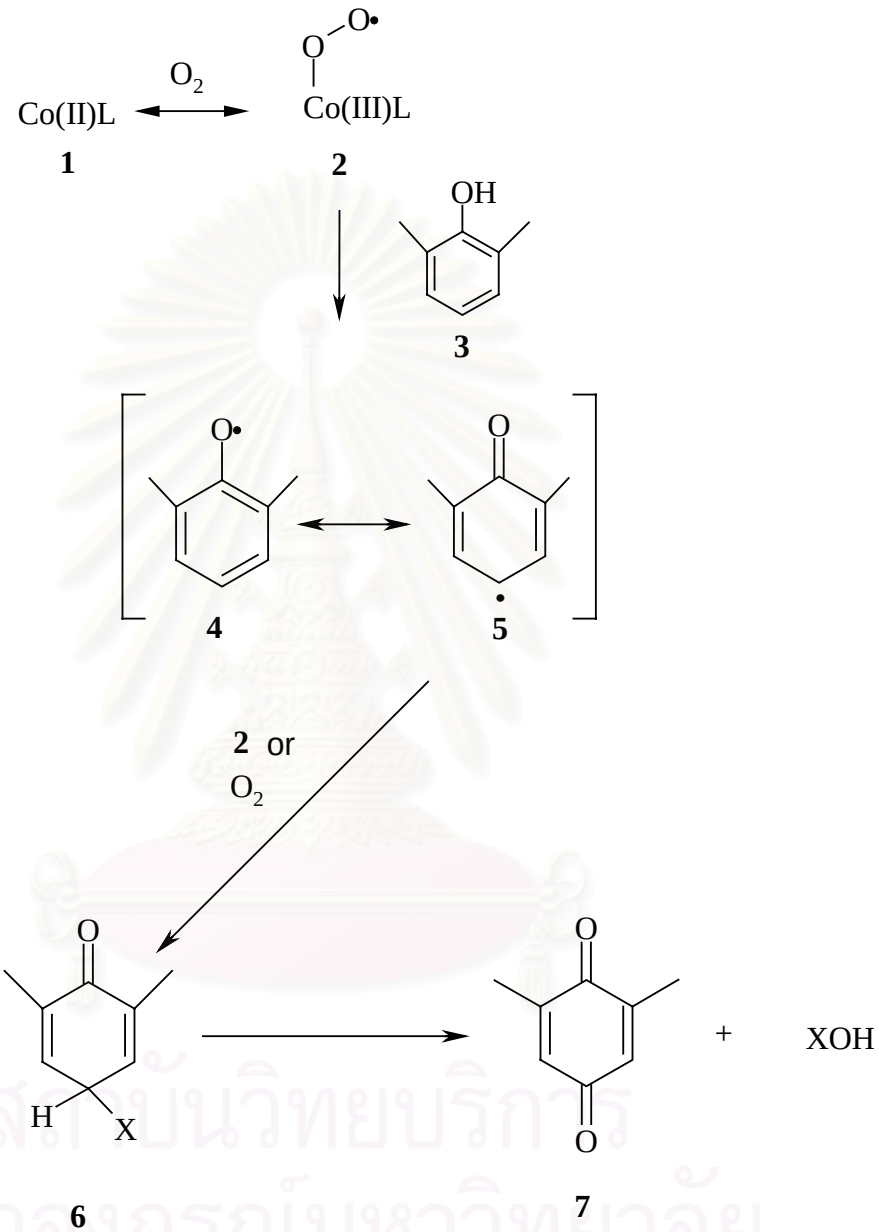
Another point could be concluded from the experiment (entry 3) that the rate of the oxidation of hydroquinone was faster than phenol, when using the same substitution. This also reinforced the idea that the more electron rich substituent would affect OH group at the *p*-position to be a good leaving group than H atom at that position.

3.6 Proposed mechanism for the oxidation of phenols to quinones catalyzed by cobalt(II)-Schiff base complexes

3.6.1 Oxygen as an oxidant

The mechanism for the Co(II)-Schiff base catalyzed oxidation of phenols was suggested that the mechanism of the Co(II)-catalyzed oxidation of phenols employing molecular oxygen as oxidant occur *via* free radical pathway.[28] The proposed mechanism is shown in Scheme 3.1.

Reaction of Co(II)-Schiff base complex with oxygen gave a superoxo Co/O_2 adduct (**2**). This complex abstracted the phenol hydrogen giving a phenoxy radical (**4** and **5**). Intermediate **5** was trapped by a second molecule of Co superoxo complex or oxygen, generating intermediate **6**. Elimination of hydrogen atom from complex **6** generated quinone **7** and, when X = Co(III)L, a Co-hydroxy species, known to be catalytically active. Alternatively, LCo(III)OOH, formed in the first step of the reaction, broke down to regenerate the starting catalyst.



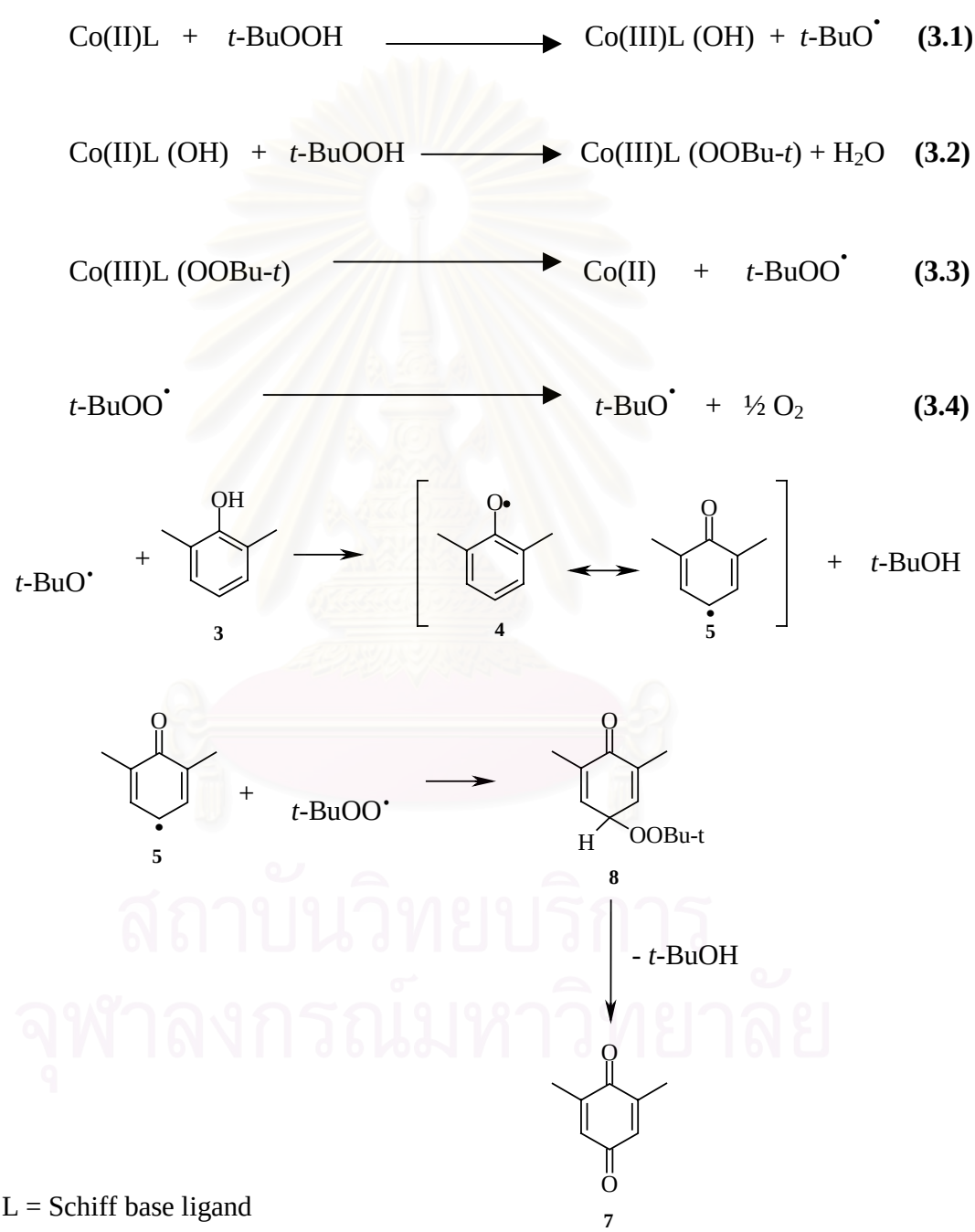
L = Schiff base ligand

X = O-O-Co(III)L or O-O•

Scheme 3.1 Proposed mechanism for the oxidation of phenols to quinones with oxygen as oxidant

3.6.2 TBHP as an oxidant

All the results described above are rationalized by the mechanism shown in Scheme 3.2, which was similar to that proposed for the Co(II)-salen catalyzed oxidation of anilines with TBHP.[38]



L = Schiff base ligand

Scheme 3.2 Proposed mechanism for the oxidation of the phenols to quinones with TBHP as oxidant

Co(II)L(OOBu-*t*) which formed rapidly in an early stage of the reaction decomposed to yield *tert*-butylperoxyl radicals (*t*-BuOO$^{\cdot}$) which gave further *tert*-butyloxy radicals (*t*-BuO$^{\cdot}$) (Scheme 3.2, eqs 3.1-3.4). The resulting oxygen radicals could react with 2,6-dimethylphenol **3** in the following way: abstracted a hydrogen atom to form the 2,6-dimethylphenoxy radicals **4** and **5.** Then intermediate **5** was trapped with *tert*-butylperoxidyl radicals to give intermediate **8.** Elimination of hydrogen atom from complex **8** generated quinone **7**.

CHAPTER IV

CONCLUSIONS

From the preceding results and discussions, the main focus of this research is to search for the optimum conditions for the oxidation of phenols catalyzed by transition metal Schiff base complexes and to develop catalytic system for the oxidation of other phenols.

The structure of Schiff base ligand, transition metal that binds with ligand, oxidizing agent, solvent system, reaction time and temperature affected the oxidation reaction. The optimum conditions for the oxidation of phenols were as follows: phenols 1.0 mmol as substrate, DMF 10 mL as solvent, oxygen as oxidant and Co(II)-salen 0.1 mmol as catalyst at room temperature for 5 hr. In addition, the optimum conditions for this reaction with TBHP as an oxidant was examined and was found that when chloroform was used as a solvent at slightly high temperature (60 ^{o}C) with 9 mmol of TBHP, the highest yield of the desired product was attained.

In term of kinetic study the results displayed that the half-life for 2,6-dimethylphenol oxidation under this optimum conditions was approximately 2 hr. The reaction was finished within 5 hr for the reaction at room temperature. In addition, when the comparative kinetic study of the oxidation of 2,6-dimethylphenol catalyzed by Co(II)-salen in the presence of DMF, THF and acetonitrile was investigated, the rate of the reaction was observed as the reaction in DMF took place faster than in acetoniutrile and in THF, respectively. The rate of the reaction at higher temperature was also faster than that at room temperature: the half-life of the reaction were approximately 2 hr at room temperature, 20 min at 40 ^{o}C and 15 min at 60^{o}C. However, the final yield of the quinone product at room temperature and higher temperature for 5 hr were almost the same.

The application of this developed oxidation reaction to other phenols was also considered. It was found that all phenols and hydroquinones used as substrates could be converted to their analogous quinones as predominant products in high yield, except for phenol, 2-chlorophenol, 2-chlorohydroquinone, 2,6-di-*tert*-butyl-4-

bromophenol, 2,4,6-tribromo-3-methyl-phenol, 2,6-dimethylaniline and anthracene that could not be converted to quinones. This finding revealed that Co(II)-salen catalyst could selectively oxidize phenols.

Suggestion for the future work

The important experiments that should be further carried out based upon this research is to develop this catalytic system to larger scale that could be applied in pilot scale of petrochemical industry. The comparative study between Co(II)-salen catalyst and other catalysts such as porphyrin complexes in the oxidation of phenols should also be studied. In addition, the variation of the functional group bearing in a substrate that could be eliminated to form radical intermediate in reaction mechanism should be investigated.

REFERENCES

1. Furniss, B.S.; Hanaford, A.J.; Smith., W.G.; and Tatchell, A.R., Vogel's, "Practical of Organic Chemistry", 5th edition, Longman Scientific and Technical, New York, 1989, p. 1019.
2. Zimner, H.; Lankin, D.C. and Horgan, S.W.,"Oxidation with Potassium Nitrosodisulfonate (Fremy's Radical). The Teuber Reaction" *Chem. Rev*., 1971, *71*, 229-246.
3. Fieser, L.F. and Fieser, M., "Reagents for Organic Chemistry", Wiley, New York, N.Y., 1986: Vol. 1, p 940.
4. Saa, J.M.; Morey, J. and Rubido, C., "An Oxidative Degradation Approach to *p*-Quinone", *J. Org. Chem.*, 1986, *51*, 4471-4473.
5. Moser, W. and Howie, R.A., "Nitrosodisulphonates. Part I. Fremy's Salt (Potassium Nitrosodisulphonate)", *J. Chem. Soc. A.*, 1968, 3039-3043.
6. Howie, R. A.; Glasser, L. S. D. and Moser, W., " Nitrosodisulphonates. Part II. Crystal Structure of the Orange-brown Triclinic Modification of Fremy's Salt (Potassium Nitrosodisulphonate)", *J. Chem. Soc. A.*, 1968, 3043-3047.
7. Haga, T., "Peroxylaminesulphonates and Hydroxylaminetrisulphonate (Sulphazilates and Metasulphazilate)", *J. Chem. Soc.*, 1904, *85*, 78-107.
8. Li, J.C.M. and Ritter, D. M., "Decomposition of Nitrosyl Disulfonate Ion. III. Reaction with Nitrous Acid and Its Reaction to the Mechanism in Acid Solution", *J. Am. Chem. Soc.*, 1952, *75*, 5823-5828.
9. Li, J.C.M. and Ritter, D. M., "Decomposition of Nitrosyl Disulfonate Ion. IV. The Reaction of Sulfamate Ion with Nitrous Acid ", *J. Am. Chem. Soc.*, 1952, *75*, 5828-5833.
10. Musso, H., "Phenol Oxidation Reactions", *Angew.Chem., Int. Ed.Engl.* 1963, *2*, 723-735.
11. Yamada, S. and Thuchida, R., "Spectrochemical Study of Microscopic Crystals. XIX The Structure and Absorption of Spectra of Fremy's Salt", *Bull. Chem. Soc. Jpn.*, 1959, *32*, 721-725.

12. Griffith, W. P.; Lewis, J. and Wilkinson, G., "Infra-red Spectra of Transition Metal-nitric Oxide Complexes-II", *J. Inorg. Nucl. Chem.*, 1958, *7*, 38-44.
13. Singh, R. P., "Preperation of Fremy's Salt , Potassium Nitrosodisulphonate", *Can. J. Chem.*, 1966, *44*, 1994-1996.
14. Salt, C. and Tomlinson, M. L., "Exhibition of Gallenkamp Apparatus", *Chem. Ind. (London)*, 1961, 549.
15. Teuber, H.–J., "The Mechanism of the Formation of Quinones from Monophenols with Dipotassium Nitrosobissulfate", *Angew.Chem., Int. Ed.Engl.* 1965, *4*, 871-872.
16. Magnusson, R., "Oxidation of Some 2,4,6-Trialkyl-substituted Phenols with Potasium Nitrosodisulfonate Part I ", *Acta Chem. Scand.*, 1964, *18*, 759-766.
17. Magnusson, R., "Oxidation of Some 2,4,6-Trialkyl-substituted Phenols with Potasium Nitrosodisulfonate Part II ", *Acta Chem. Scand.*, 1966, *20*, 2211-2214.
18. Takehira, K.; Shimizu, M.; Watanabe, Y.; Orita, H. and Hayakawa, T., "A Novel Oxygenation of 2,3,6-Trimethylphenol to Trimethyl-*p*-benzoquinone by Dioxygen with Copper(II) Chloride/Amine Hydrochloride Catalyst", *Tetrahedron Lett.*, 1989, *30*, 6691-6692.
19. Takehira, K.; Shimizu, M.; Watanabe, Y.; Orita, H. and Hayakawa, T., "A Novel Oxygenation of 2,4,6-Trimethylphenol to 3,5-Dimethyl-4-hydroxybenzaldehyde by Dioxygen with Copper(II)-Amine Complex", *Tetrahedron Lett.*, 1990, *31*, 2607-2608.
20. Orlando, C.M., Jr., "The Cuprous Chloride-Amine Catalyzed Oxidation of 2,6-Di-*t*-butyl-*p*-cresol with Oxygen", *J. Org. Chem.*, 1968, *33*, 2516-2518.
21. Shimizu, M.; Takehira, K.; Watanabe, Y.; Orita, H. and Hayakawa, T., "The Oxidation of 2,4,6-Trimethylphenol with Molecular Oxygen Catalyzed by Copper(II) Chloride-Amine System", *Bull. Chem. Soc. Jpn.*, 1993, *66*, 251-257.
22. Hewgill, F. R. and Hewitt, D. G., "Oxidation of Alkoxyphenols. VII. Cyclical Transketalisation in the Oxidation of a Mixture of Phenols", *Tetrahedron Lett.*, 1965, *42*, 3737-3739.

23. Hewgill, F. R., " Oxidation of Alkoxyphenols. XXIV. A Dipheno-2,2′-quinone from Sesamo", *Tetrahedron*, 1978, *34*, 37-39.

24. Vaska, L., "Dioxygen-metal Complexes: Toward a Unified View", *Acc. Chem. Res.*, 1976, *9*, 175-183.

25. Vogt, Jr, L.H.; Faigenbuam, H.M. and wiberley, S.E., "Synthetic Reversible Oxygen-carrying Chelates", *Chem. Rev*., 1963, *63*, 269-277.

26. Hutson, N.D. and Yang, R.T., "Synthesis and Characterization of the Sorption Properties of Oxygen-binding Cobalt Complexes Immobilized in Nanoporous Materials", *Ind. Eng. Chem. Res.*, 2000, *39*, 2252-2259.

27. Wakamatsu, T.; Nishi, T.; Ohnuma, T. amd Ran, Y., "A Convenient Synthesis of Juglone *via* Neutral Salcomine Oxidation". *Synth. Comm.*, 1984, *14*, 1167-1173.

28. Bozell, J. J. and Hames, B. R., "Cobalt-Schiff Base Complex Catalyzed Oxidation of *para*-Substituted Phenolic. Preparation of Benzoquinones", *J. Org. Chem*., 1995, *60*, 2398-2404.

29. Maruyama, K.; Kusukawa, T.; Mashino, T. and Nishinaga, A., "Co(salen)-Catalyzed *tert*-Butyl Hydroperoxide Oxidation of *tert*-Butylphenol Bearing an Unsaturated Side Chain", *J. Org. Chem*., 1996, *61*, 3342-3349.

30. Chen, D. and Martell, A.E., "Dioxygen Affinities of Synthetic Cobalt Schiff Base Complexes", *Inorg. Chem.*, 1987, *26*, 1026-1030.

31. Chavasiri, W. and Nuntasri, D., unpublished results.

32. Aminabhavi, T.M.; Rudzinski, W.E.; Biradar, S. and Patil, C.S., "Complexes of Tellurium with Vanillydene-Schiff Bases", *Inorg. Chim. Acta.*, 1983, *76*, L131-134.

33. Ho, R.K.Y. and Livengston, S.E., "Metal Complexes of Schiff base Derived from Thiophene-2-aldehyde", *Aust. J. Chem.*, 1965, *18*, 659-671.

34. Westland, A.D. and Tavafder, T.H., "Novel Peroxo Complexes of Uranium Containing Organic Ligands", *Inorg. Chem.*, 1981. *20*, 3992-.3995

35. Yomada, S. and Iwasaki, K., "Chromium (III) Complexes Containing *N,N′*-Ethylene-*bis*-(salicylideneiminate) as a Ligand", *Inorg. Chim. Acta.*, 1971, *5*, 3-5.

36. Hughes, D.L.; Kleinkes, U.; Leigh, G.J.; Maiwald, M. and Sanders, J.R., "The Preparation and Struture of $[VI_2(salen)].CH_2Cl_2$ [salen = *N*,*N*′-ethylenebis (salicylideneiminate)(2-)] and of Some Homologues of Related Schiff Bases", *J. Chem. Soc., Dalton Trans.*, 1993, 3093-3096.

37. Kessel, S.L.; Emberson, R.M.; Debrunner, P.G. and Hendrickson, D.N., "Iron(III), Manganese(III), and Cobalt(III) Complexes with Single Chelating *o*-Semiquinone Ligands", *Inorg. Chem.*, 1980, *19*, 1170.

38. Forster, S. and Rieker, A., "Cobalt Schiff Base Complex-Catalyzed Oxidation of Anilines with *tert*-Butyl Hydroperoxide", *J. Org. Chem.*, 1996, *61*, 3320-3326.

39. Pavia, D. L.; Lampman, G. M. and Kriz, G. S., "Introduction to Spectroscopy: A Guide for Students of Organic Chemistry" 2nd edition, Saunders Golden Sunburst Series, Washington, 1996, p 14.

40. Pollock, J. R. A. and Stevens, R., "Dictionary of Organic Compounds", 4th edition, London Eyre & Spottis woode. Publishers Ltd. E & F. SPON Ltd., Completely revised, enlarge and re-set edition in five volumes.

VITA

Mr. Jirasak Imurai was born on February 13, 1977 in Trad, Thailand. He recived a Bachelor's Degree of Science, majoring in Chemistry at Burapha University in 2000. Since 2000, he has been a graduate student studying in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University. He was supported by a research grant for this Master Degree's thesis from the Graduate School, Chulalongkorn University.

His present address is 109 Moo 8, Kausamink, Trad, Thailand 23130 Tel 039-537-444.