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SELECTIVE OXIDATION OF SATURATED HYDROCARBONS, ALCOHOLS
AND SULFUR- CONTAINING COMPOUNDS BY TRANSITION METAL
COMPLEXES

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ปฏิกริยาออกซิเดชันจัดเป็นปฏิกริยานิคหนึ่งที่น่าสนใจเป็นอย่างยิ่งในการเปลี่ยนรูปสารอินทรีย์ งานวิจัยนี้มุ่งเน้นที่จะศึกษาและพัฒนาระบบทัวเร่งปฏิกริยาสารประกอบเชิงช้อนของไฮเมียม โดยการศึกษานี้ใช้ไฮเมียมสเทียเรต และ ไฮเมียมพิโคลินेटในการเร่งปฏิกริยาออกซิเดชันของแอลกอฮอล์ร่วมกับ TBHP ที่อุณหภูมิ 70°C เป็นเวลา 24 ชั่วโมง ปฏิกริยาให้ปริมาณผลิตภัณฑ์ และความเสื่อมจำเพาะสูง โดยเฉพาะแอลกอฮอล์ทุกภูมิที่ไม่มีความเกลกะ สำหรับปฏิกริยาออกซิเดชันของแอลกอฮอล์ปฐมภูมิจะให้ผลิตภัณฑ์เป็นกรดcarboxylicโดยการเกิดผ่านสารประกอบแอลดีไฮด์ก่อน อย่างไรก็ตาม เมื่อใช้ตัวออกซิแดนท์อื่น เช่น ไฮโดรเจนperอิโซไซด์ หรือ โซเดียมไฮเปอร์คลอไรด์ในระบบตัวเร่งปฏิกริยาเดียวกัน ปรากฏว่าไม่สามารถเกิดปฏิกริยาออกซิเดชันของแอลกอฮอล์ได้ นอกจากนี้ภายใต้สภาวะดังกล่าว เมื่อประยุกต์ใช้กับปฏิกริยาออกซิเดชันของสารประกอบไฮโดรคาร์บอน พบร่วมปฏิกริยาเกิดขึ้นได้กับสารประกอบประเภทเบนซิลิก และเมื่อเปรียบเทียบความสามารถในการเร่งปฏิกริยา ระหว่าง ไฮเมียมสเทียเรตและไฮเมียมพิโคลินे�ตพบว่า สารประกอบเชิงช้อนของไฮเมียมทั้งสองให้ผลในการเร่งปฏิกริยาไม่ต่างกัน แต่ไฮเมียมพิโคลินे�ตสามารถแยกออกจากปฏิกริยาได้ง่ายกว่า และสำหรับปฏิกริยาออกซิเดชันของสารที่มีกำมะถันเป็นองค์ประกอบ ปฏิกริยาเกิดขึ้นอย่างรวดเร็วจึงเหมาะสมที่จะประยุกต์ใช้ในกระบวนการกำจัดสารประกอบกำมะถันในสิ่งแวดล้อม ปฏิกริยาออกซิเดชันที่ได้พัฒนาขึ้นนี้เชื่อว่าเกิดผ่านกระบวนการฟรีเอดิคเลต

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UTHUMPORN THONG-IN: SELECTIVE OXIDATION OF SATURATED HYDROCARBONS, ALCOHOLS AND SULFUR-CONTAINING COMPOUNDS BY TRANSITION METAL COMPLEXES: ASST. PROF. WARINTHORN CHAVASIRI, Ph.D., 125 pp. ISBN 974-14-3373-5.

Oxidation reactions are interesting for functionalization of organic compounds and remain a reaction of considerable value in organic synthesis. This study focuses on the development of a catalytic system based on chromium catalysts. For this research, chromium(III) stearate and chromium(III) picolinate catalysts were utilized for the first time with *tert*-butyl hydroperoxide as an oxidant for the oxidation of alcohols. This reaction was achieved at 70°C for 24 h and the corresponding carbonyl compounds were obtained in high yield with good selectivity especially for secondary alcohols without steric hindrance. The oxidation of primary alcohols afforded the corresponding carboxylic acids *via* aldehydes. Otherwise, the use of other oxidants such as hydrogenperoxide or sodium hypochorite afforded the unnecessary ability for the alcohol oxidations. After the optimized condition was established, this oxidation system was applied to the oxidation of various hydrocarbons. This catalytic oxidation also expressed good results for the oxidation at a benzylic position. Chromium(III) stearate and chromium(III) picolinate expressed comparable activity toward oxidation reaction, however chromium(III) picolinate was easy to separate from the reaction medium. This developed system was also appropriate for the oxidation of sulfur containing compounds. The outcome revealed that this system was suited to be employed as chemical remediation process in environmental viewpoint. These developed chromium(III) catalyst oxidation systems were believed to undergo *via* a free radical process.

Field of study Petrochemistry

Academic year.....2005..... Student's signature.....*Uthumporn Thong-in*.....

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LIST OF ABBREVIATIONS

AcOH	acetic acid
anh	anhydrous
aq	aqueous
atm	atmosphere
b	broad (IR)
b.p.	boiling point
BTF	benzotrifluoride
°C	degree celsius
CHP	cumene hydroperoxide
cm ⁻¹	unit of wavenumber
Cr(acac) ₃	chromium(III) acetylacetone
Cr(bza) ₃	chromium(III) benzoylacetate
Cr(cur) ₃	chromium(III) curcumin
Cr(pic) ₃	chromium(III) picolinate
Cr(str) ₃	chromium(III) stearate
d	doublet (NMR)
dd	doublet of doublet (NMR)
eq	equivalent (s)
equiv	equivalent (s)
Fig	Figure
g	gram (s)
GC	gas chromatography
h	hour(s)
Hz	hertz
IR	infrared
<i>J</i>	coupling constant (NMR)
m	multiplet (NMR)
m	moderate (IR)
MeCN	acetoneonitrile
min	minute(s)

mL	milliliter (s)
mmol	millimole (s)
m.p.	melting point
N-Boc	<i>N-tert</i> -butoxy-carbonyl
NMR	nuclear magnetic resonance
OAc	acetate
PCC	pyridinium chlorochromate
PhIO	iodozobenzene
ppm	part per million
py	pyridine
q	quartet (NMR)
quar	quartet (NMR)
quint	quintet (NMR)
R _f	retardation factor singlet (NMR)
RT	room temperature
s	singlet (NMR)
s	strong (IR)
t	triplet (NMR)
TBHP	<i>tert</i> -butyl hydroperoxide
t-BuOOH	<i>tert</i> -butyl hydroperoxide chemical shift (NMR)
TEMPO	2,2,6,6-tetramethylpiperidinoxy
TLC	thin layer chromatography
w	weak (IR)
%	percentage