

เคมีแสงของ 1-เมทิลไพราโซลที่มีหมู่แทนที่ไทรฟลูออโรเมทิล

นาย เทพวุฒิ อิศรเสนา ณ อยุธยา



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาเคมี ภาควิชาเคมี

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2545

ISBN 974-17-1509-9

ลิขสิทธิ์ของ จุฬาลงกรณ์มหาวิทยาลัย

**PHOTOCHEMISTRY OF TRIFLUOROMETHYL  
SUBSTITUTED-1-METHYLPYRAZOLES**

**Mr. Theppawut Israsena Na Ayudhya**

**A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science in Chemistry**

**Department of Chemistry**

**Faculty of Science**

**Chulalongkorn University**

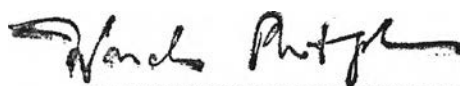
**Academic Year 2002**

**ISBN 974-17-1509-9**

**Thesis Title** PHOTOCHEMISTRY OF TRIFLUOROMETHYL  
SUBSTITUTED-1-METHYLPYRAZOLES  
**By** Mr. Theppawut Israsena Na Ayudhya  
**Field of Study** Chemistry  
**Thesis Advisor** Associate Professor Supawan Tantayanon, Ph.D.  
**Thesis Co-Advisor** Professor James W. Pavlik


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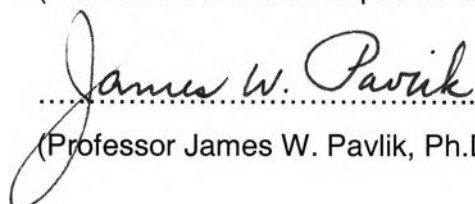
Accepted by the Faculty of Science, Chulalongkorn University in Partial  
Fulfillment of the Requirement for the Master's Degree

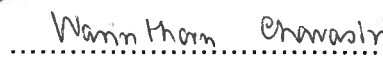
  
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..... Chairman  
(Associate Professor Sophon Roengsumran, Ph.D.)

  
..... Thesis Advisor  
(Associate Professor Supawan Tantayanon, Ph.D.)

  
..... Thesis Co-Advisor  
(Professor James W. Pavlik, Ph.D.)

  
..... Member  
(Assistant Professor Warintorn Chavasiri, Ph.D.)

  
..... Member  
(Assistant Professor Worawan Bhanthumnavin, Ph.D.)

เทพวุฒิ อิศรเสนา ณ อยุธยา : เคมีแสงของ 1-เมทิลไพราโซลที่มีหมู่แทนที่ไทรฟลูออโรเมทิล (PHOTOCHEMISTRY OF TRIFLUOROMETHYL SUBSTITUTED-1-METHYLPYRAZOLES) อาจารย์ที่ปรึกษา : รศ. ดร. ศุภวรรณ ดันตยานนท์, อาจารย์ที่ปรึกษา  
ร่วม : PROFESSOR JAMES W. PAVLIK, จำนวนหน้า 120 หน้า. ISBN 974-17-1509-9.

งานวิจัยนี้เป็นการตรวจสอบปฏิกิริยาเคมีแสงของสารกลุ่ม 1-เมทิลไพราโซลที่มีหมู่แทนที่ไทรฟลูออโรเมทิล 3-, 4- และ 5-ไทรฟลูออโรเมทิล-1-เมทิลไพราโซลได้ถูกสังเคราะห์และศึกษาพฤติกรรมทางเคมีแสงของสารเหล่านี้ ผลิตภัณฑ์ที่คาดว่าจะเกิดขึ้นได้แก่ 2-, 4- และ 5-ไทรฟลูออโรเมทิล-1-เมทิลอิมิดาโซล ได้ถูกสังเคราะห์ขึ้นด้วย ได้ทำปฏิกิริยาของแสงโดยใช้แหล่งของแสงที่เหมาะสมและตรวจสอบโดย จีซี-เอฟไอดี และ จีซี-เอ็มเอส การบ่งชี้ผลิตภัณฑ์ทำโดยการเปรียบเทียบข้อมูลทางโครมาโทกราฟี และ แมสสเปกโทรเมทริกกับสารจริง เมื่อทำการฉายแสงให้แก่ 1-เมทิล-3-ไทรฟลูออโรเมทิลไพราโซล ผลของปฏิกิริยาบ่งชี้ว่าเกิด 1-เมทิล-2-ไทรฟลูออโรเมทิลอิมิดาโซล และ 1-เมทิล-4-ไทรฟลูออโรเมทิลอิมิดาโซล ขึ้นโดยผ่านการปัดวงแบบอเล็กโตรไซคลิก สารชนิดหลังเป็นผลิตภัณฑ์ที่สองที่เกิดจาก 1-เมทิล-2-ไทรฟลูออโรเมทิล-อิมิดาโซล ปฏิกิริยาเคมีแสงของ 1-เมทิล-4-ไทรฟลูออโรเมทิลไพราโซลให้ 1-เมทิล-4-ไทรฟลูออโรเมทิลอิมิดาโซลเท่านั้น ในปฏิกิริยามีอินเทอร์มีเดียตที่เกิดจากการแตกออกด้วยแสงซึ่งถูกบ่งชี้ว่าเป็น ซิส และ ทรานส์ไอโซเมอร์ของ 3-N-เมทิลเอมิโน-2-ไทรฟลูออโรเมทิลโพรพีนไนไตรด์ และ N-เมทิลเอมิโน-1-ไทรฟลูออโรเมทิลเอทิลไอโซไซยาไนด์ ซึ่งตรวจสอบได้ด้วย โพรตอนเอ็นเอ็มอาร์ และ อินฟราเรดสเปกโทรสโกปี เมื่อ 1-เมทิล-5-ไทรฟลูออโรเมทิลไพราโซล ถูกฉายแสงสารจะแตกออกด้วยแสงเป็น 1-เมทิล-5-ไทรฟลูออโรเมทิลอิมิดาโซล และ ปัดวงแบบอเล็กโตรไซคลิกเป็น 1-เมทิล-2-ไทรฟลูออโรเมทิลอิมิดาโซล และ 1-เมทิล-4-ไทรฟลูออโรเมทิลอิมิดาโซล โดยการใช้เทคนิคโพรตอนเอ็นเอ็มอาร์ และ อินฟราเรด สเปกโทรสโกปี สรุปได้ว่ามีอินเทอร์มีเดียตที่เกิดจากการแตกออกด้วยแสงของปฏิกิริยานี้คือ ซิส และ ทรานส์ไอโซเมอร์ คือ N-เมทิลเอมิโน-3-ไทรฟลูออโรเมทิลโพรพีนไนไตรด์ และ 2-N-เมทิลเอมิโน-2-ไทรฟลูออโรเมทิลเอทิลไอโซไซยาไนด์

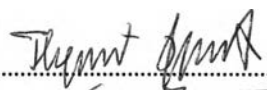
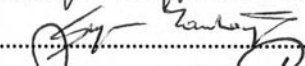
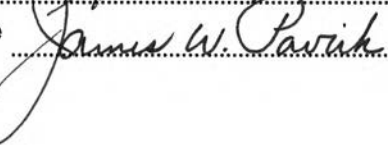
ภาควิชา.....เคมี.....ลายมือชื่อนิสิต *Thyunt Anuk*  
สาขาวิชา.....เคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา *James W. Pavlik*  
ปีการศึกษา.....2545.....ลายมือชื่ออาจารย์ที่ปรึกษาร่วม *James W. Pavlik*

# # 4473812823:MAJOR CHEMISTRY

KEY WORD :TRIFLUOROMETHYL SUBSTITUTED-1-METHYLPYRAZOLES,ELECTROCYCLIC, SIGMATROPIC SHIFT, PHOTOTRANSPOSITION

THEPPAWUT ISRASENA NA AYUDHYA: PHOTOCHEMISTRY OF TRIFLUOROMETHYL SUBSTITUTED-1-METHYLPYRAZOLES, THESIS ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., THESIS CO-ADVISOR: PROF. JAMES W. PAVLIK, Ph.D., 120 pp. ISBN 974-17-1509-9.

This research involves the exploration in the photochemical reaction of trifluoromethyl substituted-1-methylpyrazoles. The 3-, 4-, and 5-(trifluoromethyl)-1-methylpyrazoles were synthesized and their photochemical behaviors were investigated. The photoreactions were carried out with appropriate light sources and monitored by GC-FID and GC-MS. The product identification was performed by the comparison of their chromatographic and mass spectroscopic data with the authentic samples. Some anticipated products, such as 2-, 4-, and 5-(trifluoromethyl)-1-methylimidazoles, were also synthesized. Upon irradiation of 1-methyl-3-(trifluoromethyl)pyrazole, the result indicated the generation of 1-methyl-2-(trifluoromethyl)imidazole and 1-methyl-4-(trifluoromethyl)imidazole via electrocyclic ring closure. The latter was assumed to be the secondary product arising from 1-methyl-2-(trifluoromethyl)imidazole. The photoreaction of 1-methyl-4-(trifluoromethyl)pyrazole afforded only 1-methyl-4-(trifluoromethyl)imidazole. In this reaction the photocleavage intermediates, which were identified as *cis*- and *trans*-isomers of 3-(*N*-methylamino)-2-(trifluoromethyl)propenenitrile and (*N*-methylamino)-1-(trifluoromethyl)ethenylisocyanide, were detected by <sup>1</sup>H-NMR and infrared spectroscopy. When 1-methyl-5-(trifluoromethyl)pyrazole was irradiated, it underwent photocleavage to 1-methyl-5-(trifluoromethyl)imidazole, as well as electrocyclic ring closure to 1-methyl-2-(trifluoromethyl)imidazole and 1-methyl-4-(trifluoromethyl)imidazole. By using <sup>1</sup>H-NMR spectroscopic technique, it could be concluded that the photocleavage intermediates of this reaction were *cis*- and *trans*- isomers of (*N*-methylamino)-3-(trifluoromethyl)propenenitrile and 2-(*N*-methylamino)-3-(trifluoromethyl)ethenylisocyanide.

Department	Chemistry	Student's signature	
Field of study	Chemistry	Advisor's signature	
Academic year	2002	Co-advisor's signature	



## ACKNOWLEDGEMENT

The author wishes to express deepest gratitude to his advisor, Associate Professor Supawan Tantayanon and his co-advisor, Professor James W. Pavlik, for their generous guidance, helpful suggestions, and encouragement throughout the course of this research. He also thanks the chairman and members of the thesis committee for their valuable suggestions and comments.

He acknowledges financial support from The Development and Promotion of Science and Technology Talent Project and Tab Neelanithi Foundation, Bangkok, Thailand. He wishes to express grateful thanks to Worcester Polytechnic Institute for provision of teaching assistantship and for giving him a chance to be teaching assistant in The United States of America.

The author also would like to express his gratitude to First Lady Tinaprapa Israsena Na Ayudhya and First Lady Thudsanee Bhunyakubta for their love and encouragement.

Finally, thanks go towards to Mr. Somchoke Launhasurayotin and Miss Nantanit Wanichacheva, other Thai students, and Hubert for transportation, food and funny times in Worcester, Vikki, Starla, Emily, and Jenny for keep talking with talkative guy like me, and all of graduate students in Chemistry Department at WPI for fantastic party and funny soccer games even though Turkish guys always came late.

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cm <sup>-1</sup>	unit of wavenumber
°C	degree celsius
d	doublet
dd	doublet of doublet
dt	doublet of triplet
FID	flame ionization detector
FT	fourier transform
GC	gas chromatography
Hg	mercury
IR	infrared
J	coupling constant
M	multiplet
m/z	mass per charge
mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
ppm	parts per million
q	quartet
s	singlet
t	triplet
THF	tetrahydrofuran
W	watt
ε	extinction coefficient
δ	chemical shift