

วิธีสังเคราะห์พันธะคาร์บอน-คาร์บอนและคาร์บอน-เฮเทอโรอะตอมโดยใช้ฟอสฟอรัสรีเอเจนต์

นายวันชัย ปลื้มภาณุภัทร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต

สาขาวิชาเคมี ภาควิชาเคมี

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2548

ISBN 974-14-1830-2

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

SYNTHETIC METHOD FOR CARBON-CARBON AND CARBON-  
HETEROATOM BONDS USING PHOSPHORUS REAGENTS

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A Dissertation Submitted in Partial Fulfillment of the Requirements  
for the Degree of Doctor of Philosophy Program in Chemistry

Department of Chemistry

Faculty of Science

Chulalongkorn University

Academic Year 2005


ISBN 974-14-1830-2

481619

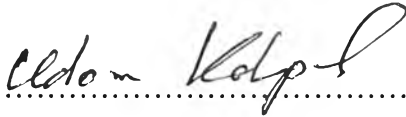
Thesis Title            Synthetic Method for Carbon-Carbon and Carbon-Heteroatom  
                              Bonds Using Phosphorus Reagents  
By                         Mr. Wanchai Pluempanupat  
Field of Study         Chemistry  
Thesis Advisor        Assistant Professor Warinthorn Chavasiri, Ph.D.

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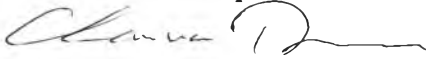
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วันชัย ปลื้มภาณุภัทร: วิธีสังเคราะห์พันธะคาร์บอน-คาร์บอนและคาร์บอน-เฮเทอโรอะตอม โดยใช้ฟอสฟอรัสรีเอเจนต์ (SYNTHETIC METHOD FOR CARBON-CARBON AND CARBON-HETEROATOM BONDS USING PHOSPHORUS REAGENTS)  
 อ. ที่ปรึกษา: ผศ. ดร. วรินทร์ ชวศิริ, 156 หน้า. ISBN 974-14-1830-2.

ได้ค้นพบวิธีการสังเคราะห์พันธะคาร์บอน-คาร์บอนและคาร์บอน-เฮเทอโรอะตอมโดยใช้ฟอสฟอรัสรีเอเจนต์ แบบใหม่และมีประสิทธิภาพ

1) ออกซิเดชัน-รีดักชัน คอนเดนเซชันระหว่าง 2-ซัลฟานิล-1,3-เบนโซไทเอซอล (HSBtz) และเทอร์เชียรีแอลคิลไคเฟนิลฟอสไฟน์ สามารถเกิดขึ้นได้อย่างมีประสิทธิภาพโดยมีแคมฟอร์ควิโนน ซึ่งเป็นสารออกซิแดนซ์ชนิดใหม่อยู่ด้วย ได้ผลผลิตซัลไฟด์ในปริมาณสูง ผ่านการแทนที่แบบ  $S_N2$  เมื่อกำจัดหมู่ Btz ของผลิตภัณฑ์ เอส-แอลคิลเลชันออกจะได้ไคแอลคิลซัลไฟด์

2) ได้ค้นพบรีเอเจนต์ผสมระหว่างแอลคิลไคเฟนิลฟอสไฟน์และ 2,6-ได-เทอร์เชียรีบิวทิล-1,4-เบนโซควิโนน (DBBQ) เพื่อใช้เป็นแนวทางการสังเคราะห์ใหม่สำหรับการสร้างพันธะคาร์บอน-คาร์บอน คอนเดนเซชันที่มี DBBQ เป็นตัวชักนำของไพรมารีและเซคันดารี แอลคิลไคเฟนิลฟอสไฟน์กับสารประกอบเมทิลีนที่มีความว่องไว เช่น (เฟนิลซัลโฟนิล)เอซีโทไนทริล, บิส(เฟนิลซัลโฟนิล)มีเทน และไคเบนซิลมาโลเนท ได้ผลิตภัณฑ์ ซี-แอลคิลเลเทต ในปริมาณปานกลางจนถึงสูงที่อุณหภูมิห้อง

3) คลอรีเนชันของแอลกอฮอล์โดยใช้รีเอเจนต์ผสมใหม่ระหว่างไตรเฟนิลฟอสฟีน ( $PPh_3$ ) และไตรคลอโรแอะเซตามิด ( $Cl_3CCONH_2$ ) ให้แอลคิลคลอไรด์ที่สอดคล้องกันในปริมาณสูง ภายใต้ภาวะที่ไม่รุนแรง ระยะเวลาสั้น พบว่าไพรมารีแอลกอฮอล์ว่องไวต่อ  $Cl_3CCONH_2/PPh_3$  มากที่สุด และให้แอลคิลคลอไรด์ทั้งหมด เชื่อว่ากลไกการเกิดปฏิกิริยาเกิดผ่านการแทนที่แบบ  $S_N2$  โดยมีหลักฐานสนับสนุนจากการได้ผลิตภัณฑ์แอลคิลคลอไรด์ที่มีคอนฟิกูเรชันแบบอินเวอร์ชัน

ภาควิชา.....เคมี.....

สาขาวิชา.....เคมี.....

ปีการศึกษา.....2548.....

ลายมือชื่อนิสิต.....วันชัย ปลื้มภาณุภัทร.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....วรินทร์ ชวศิริ.....

## 4473834623: MAJOR CHEMISTRY

KEY WORD: OXIDATION-REDUCTION CONDENSATION/ HALOGENATED REAGENTS/ ALKYL DIPHENYLPHOSPHINITES

WANCHAI PLUEMPANUPAT: SYNTHETIC METHOD FOR CARBON-CARBON AND CARBON-HETEROATOM BONDS USING PHOSPHORUS REAGENTS. THESIS ADVISOR: ASST. PROF. WARINTHORN CHAVASIRI, Ph.D., 156 pp. ISBN 974-14-1830-2.

A novel and efficient synthetic method for carbon-sulfur, carbon-carbon and carbon-chlorine bonds using phosphorus reagents was disclosed.

1) Oxidation-reduction condensation between 2-sulfanyl-1,3-benzothiazole (HSBtz) and tertiary alkyl diphenylphosphinites could smoothly be proceeded in the presence of camphor quinone (CPQ) as a new oxidant to furnish the corresponding sulfide in good yields *via*  $S_N2$  displacement. Subsequent removal of the Btz groups of *S*-alkylated products provided dialkyl sulfides.

2) The combination of alkyl diphenylphosphinites and 2,6-di-*tert*-butyl-1,4-benzoquinone (DBBQ) was disclosed as a new synthetic route for carbon-carbon bond formation. The DBBQ-induced condensation of primary and secondary alkyl diphenylphosphinites with active methylene compounds such as (phenylsulfonyl)acetonitrile, *bis*(phenylsulfonyl)methane and dibenzyl malonate proceeded smoothly at room temperature to form the *C*-alkylated products in moderate to high yields.

3) The chlorination of alcohols utilizing a new combination of triphenylphosphine ( $PPh_3$ ) and trichloroacetamide ( $Cl_3CCONH_2$ ) furnished the corresponding alkyl chlorides in high yield under mild conditions within short reaction time. Primary alcohols appear to be the most reactive substrate towards  $Cl_3CCONH_2/PPh_3$  yielding exclusively the corresponding chlorides. The general mechanism was believed to occur *via*  $S_N2$  supporting by the evidence of the inversion of configuration of the analogous alkyl chloride.

Department.....Chemistry.....

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Field of study.....Chemistry.....

Advisor's signature.....Warinthorn Chavasiri

Academic year.....2005.....

## ACKNOWLEDGEMENTS

The author would like to express his deep appreciation to his advisor, Assistant Professor Dr. Warinthorn Chavasiri for his very kind assistance, generous guidance, and encouragement throughout the course of this research. Sincere thanks are extended to Natural Products Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University for the support of chemicals and laboratory facilities and Chulalongkorn University for the HM. King Rama IX 72th Anniversary scholarship. In addition, the author also wishes to express gratitude to Professor Dr. Udom Kokpol, Professor Dr. Padet Sidisunthorn, Associate Professor Dr. Nuanphun Chantarasiri, Associate Professor Dr. Supanna Techasakul and Assistant Professor Dr. Chamnan Patarapanich serving as the chairman and members of this thesis committee, respectively, for their valuable discussion and suggestion.

The author also acknowledged Professor Dr. Teruaki Mukaiyama and Kazuhiro Ikegai, Center for basic research, the Kitasato institute, Toshima, Kita-ku, Tokyo, Japan, for providing the knowledge and practical skill on a new methodology study for the preparation of carbon-sulfur and carbon-carbon bond formations by oxidation-reduction condensation.

The author would also like to express his special thanks to gratitude to his parents, family members and Miss Sujitra Deesamer for their inspiration, understanding, great support and encouragement throughout the entire course of study. Finally his great thanks are expanded to all of his friends and member in Natural Products Research Unit for their friendship, helps and limitless effort during his graduate studies. Without them, the author would never have been able to achieve this goal.

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## LIST OF ABBREVIATIONS

|                                 |   |
|---------------------------------|---|
| %                               | percent                                     |
| °C                              | degree of Celsius                           |
| Å                               | angstrom                                    |
| Σ                               | mass balance                                |
| anh                             | anhydrous                                   |
| β                               | beta  |
| BQ                              | 1,4-benzoquinone                            |
| Bz                              | benzoyl                                     |
| Bn                              | benzyl                                      |
| CDCl <sub>3</sub>               | deuterate chloroform                        |
| CH <sub>2</sub> Cl <sub>2</sub> | dichloromethane                             |
| CHCl <sub>3</sub>               | chloroform                                  |
| cm                              | centimeter                                  |
| cm <sup>-1</sup>                | unit of wavelength                          |
| CPQ                             | camphor quinone                             |
| d                               | doublet (NMR)                               |
| DBBQ                            | 2,6-di- <i>tert</i> -butyl-1,4-benzoquinone |
| dd                              | doublet of doublet (NMR)                    |
| DEAD                            | diethyl azo dicarboxylate                   |
| DMBQ                            | 2,6-dimethyl-1,4-benzoquinone               |
| DMSO                            | dimethylsulfoxide                           |
| eq                              | equivalent                                  |
| Et <sub>2</sub> O               | diethyl ether                               |
| EtOAc                           | ethyl acetate                               |
| Fig                             | figure                                      |
| FT                              | fourier transform                           |
| γ                               | gamma                                       |
| g                               | gram (s)                                    |
| h                               | hour (s)                                    |
| HME                             | hydroquinone monobenzyl ether               |

|          |                                       |
|----------|---------------------------------------|
| HSBtz    | 2-sulfanyl-1,3-benzothiazole          |
| Hz       | hertz                                 |
| IR       | infrared                              |
| <i>J</i> | coupling constant                     |
| M        | molar                                 |
| m        | multiplet (NMR)                       |
| m.p.     | melting point                         |
| mg       | milligram (s)                         |
| min      | minute (s)                            |
| mL       | milliliter                            |
| mm       | millimeter                            |
| mmol     | millimole                             |
| MS       | molecular sieve                       |
| MW       | molecular weight                      |
| nm       | nanometer                             |
| NMR      | nuclear magnetic resonance            |
| ppm      | part per million                      |
| PTLC     | preparative thin layer chromatography |
| q        | quatet (NMR)                          |
| quant    | quantitative                          |
| quin     | quintet (NMR)                         |
| RT       | room temperature                      |
| s        | singlet (NMR)                         |
| sex      | sextet (NMR)                          |
| t        | triplet (NMR)                         |
| TfOH     | trifluoromethane sulfonic acid        |
| THF      | tetrahydrofuran                       |
| TLC      | thin layer chromatography             |
| UV       | ultra violet                          |
| vol      | volume                                |
| wt       | weight                                |
| $\alpha$ | alpha                                 |
| $\delta$ | chemical shift                        |

|               |               |
|---------------|---------------|
| $\lambda$     | wavelength    |
| $\mu\text{g}$ | microgram (s) |
| $\mu\text{M}$ | micromolar    |