

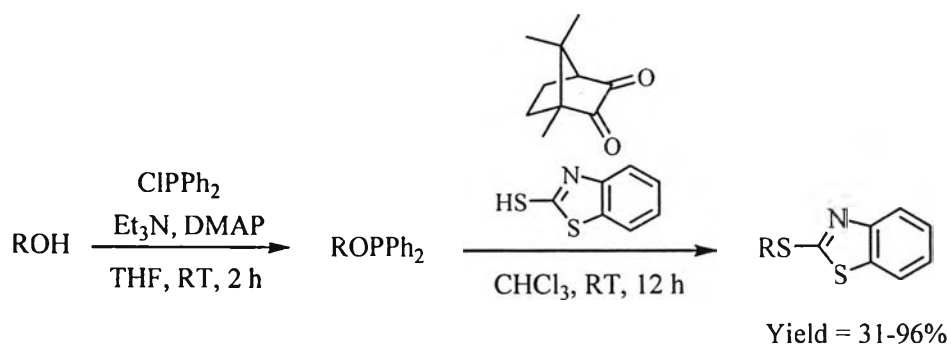
CHAPTER IV

CONCLUSION

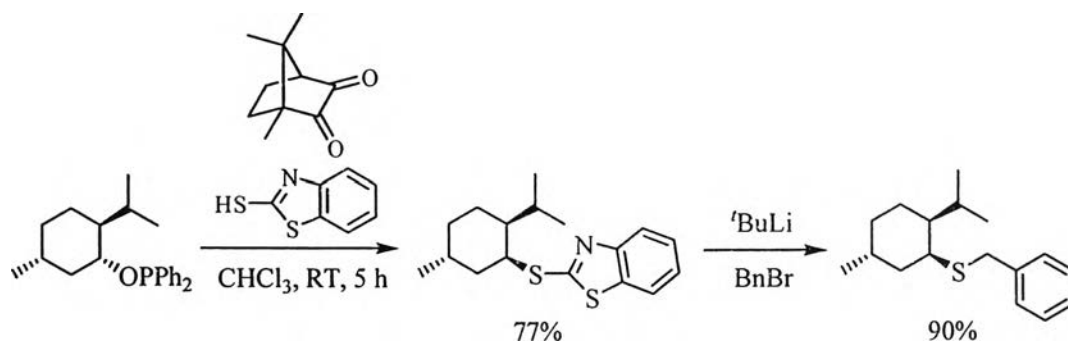
This research is to investigate and to develop the new methodology for carbon-carbon and carbon-heteroatom bond formations using phosphorus reagent. Phosphorous compounds are employed in the combination with quinone derivatives or halogenated reagents to generate a wide variety of useful reagents which can be summarized as follows:

4.1 Carbon-Sulfur Bond Formation

Oxidation-reduction condensation between 2-sulfanyl-1,3-benzothiazole and tertiary alkyl diphenylphosphinites, prepared from tertiary alcohols on treatment with ClPPh_2 in the presence of Et_3N and a catalytic amount of DMAP, can be smoothly proceeded in the presence of CPQ to furnish the corresponding *S*-alkylated products in good yields *via* $\text{S}_{\text{N}}2$ displacement.

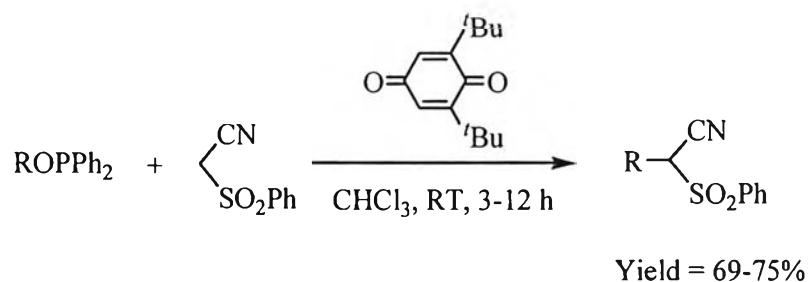


Subsequent removal of the Btz groups of *S*-alkylated products with $t\text{BuLi}$ and then BnBr provided to dialkyl sulfides. It is interesting to note that this method enabled to manipulate the *S*-alkylation of chiral alcohols with successfully inversion of configuration.



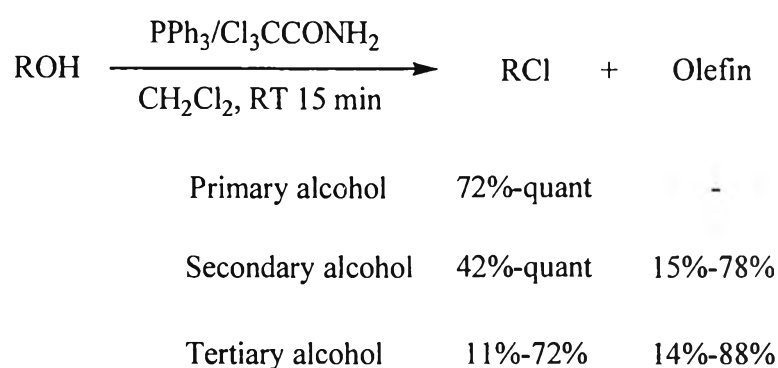
4.2 Carbon-Carbon Bond Formation

It is noted that a new-type of oxidation-reduction condensation of alkyl diphenylphosphinites with active methylene compounds such as (phenylsulfonyl)acetonitrile, *bis*(phenylsulfonyl)methane and dibenzyl malonate was performed by using DBBQ. The DBBQ-mediated condensation of primary and secondary alkyl diphenylphosphinites with (phenylsulfonyl)acetonitrile could be proceeded smoothly at room temperature to form the C-alkylated products in moderate to high yields. Moreover, the reactions using 1,4-benzoquinone derivatives were influenced by the bulky substituents at 2- and 6-positions which prevented side reactions such as alkylation of the phenoxide anion adduct.



4.3 Carbon-Chlorine Bond Formation

The chlorination of alcohols utilizing a new combination of $\text{PPh}_3/\text{Cl}_3\text{CCONH}_2$ could be smoothly converted to the corresponding alkyl chlorides in high yield under mild conditions within short reaction time. Primary alcohols appear to be the most reactive substrate towards $\text{PPh}_3/\text{Cl}_3\text{CCONH}_2$ yielding exclusively the corresponding chlorides *via* $\text{S}_{\text{N}}2$ displacement. However, the steric hindrance of secondary or tertiary alcohols strongly affects to afford a low desired chloride and consequently to a large production of olefin.



4.4 Proposal for the Future Work

This research concerned with the new and efficient route for the synthesis of carbon-carbon and carbon-heteroatom bonds using phosphorus reagents. From the academic view point, bioactive compounds and pharmaceutically active compounds containing chiral center are interesting to synthesize starting from alcohols under developed conditions.

Moreover, there are many prospective points that could be further carried out based upon the outcome originated from carbon-chlorine bond formation study. For instance, the chlorinated reagents with electron-withdrawing group provided alkyl chloride in high yield. Therefore, other brominated and iodinated reagents bearing electron-withdrawing group such as Br_3CCN , $\text{Br}_3\text{CCOCBr}_3$ and $\text{ICH}_2\text{CO}_2\text{Et}$ for the preparation of carbon-bromine and carbon-iodine bond formation using phosphorus reagents should be mediated to study the characteristic of developed reagent. Besides, a variety of alcohols such as allylic or benzylic alcohols effects also should be cautiously investigated. Thus, the controlled selectivity of the chlorination under $\text{PPh}_3/\text{Cl}_3\text{CCONH}_2$ is also another important point crucially needed to be evaluated.