

3231036 SCOC/D : MAJOR : ORGANIC CHEMISTRY; Ph.D. (Organic Chemistry)
 : OXY-BENZYLISOQUINOLINE/HYPERVALENT ORGANOIODINES
 THOSAPORN RITWIRUNE : I. SYNTHESIS AND CHEMICAL TRANSFORMATION
 OF OXY-BENZYLISOQUINOLINE ALKALOIDS II. SYNTHETIC UTILITIES OF
 HYPERVALENT ORGANOIODINE REAGENTS : APPLICATIONS TO THE SYNTHESIS OF
 SOME ALKALOID DERIVATIVES. THESIS ADVISOR : SOMSAK RUCHIRAWAT Ph.D.,
 AMORNSRI CHERMPRAPAI Ph.D., SUNANTA VIBULJAN Ph.D., SUPALUK
 PRACHAYASITTIKUL Ph.D., SOMYOIE SUTTHIVAIYAKIT Ph.D. 394 p. ISBN 974-661-511-4

In Chapter I, α -hydroxybenzylisoquinolines were synthesized by various methods: (i) reduction of 1-benzoylisoquinolines with sodium borohydride (ii) metalations of *N*-formamidine derivatives, BF_3 complex and BH_3 complex of the tetrahydroisoquinoline derivatives, as well as the application of Reissert compounds. In addition, the preparation of α -hydroxybenzylisoquinolines chromium(0) complexes was also investigated. It was found that such complexes could only be obtained from the metalation reaction of BF_3 complex of the simple tetrahydroisoquinolines. Furthermore, the reactions of the α -hydroxybenzylisoquinolines with formic acid or with iodotrimethylsilane were studied. It was found that 1-(3,4-dimethoxyphenyl)-3-substituted-7,8-dimethoxy-1,2,4,5-tetrahydro-3H-[3]benzazepines could be synthesized from the reactions of α -hydroxybenzyltetrahydroisoquinolines having secondary amine moieties and substrates of *N*-methyl or *N*-benzyl-1,2,3,4-tetrahydropapaverinol. However, in the case of the starting α -hydroxybenzylisoquinoline compounds containing the oxygenated aromatic moieties on the *N*-benzyl ring, the protoberberine alkaloids were found to be the products of the reaction. In addition, α -hydroxybenzylisoquinoline chromium(0) complexes were found to resist the transformation to 1-phenyl-3-methylbenzazepine.

For chapter II, synthetic application of hypervalent organoiodines such as (diacetoxyiodo)benzene (DIB) and [bis(trifluoroacetoxy)iodo]benzene (BTI) for the syntheses of some interesting alkaloids was studied. As a result, we have developed an approach to the syntheses of 1-aryloxyisoquinoline alkaloids, employing the BTI oxidation of the 3,4-dihydroisoquinoline alkaloids affording high yield of 1-aryloxy-3,4-dihydroisoquinolines. In addition, various enamide derivatives were found to react with DIB or BTI to furnish oxazoline derivatives. It was found that the oxidation of urethane enamides gave the oxazolidone derivatives, but when simple enamides were used as starting materials, hydroxy oxazolines were instead obtained from the reaction. Moreover, it was found the application of DIB or BTI for the high yield synthesis of glaucine and neospirinedienone *via* the intramolecular coupling of nonphenolic benzylisoquinolines. In the case of BTI oxidation of tetrahydroisoquinoline lacking 3,4-dimethoxy groups on benzyl moiety, the iminium salts were achieved as products. However, phenylisoquinoline derivatives were oxidized under similar condition to form the phenyl iminium salt. In addition, papaverinol was oxidized by BTI to yield the fragmented aldehyde product.