



CHAPTER IV

CONCLUSION

The purpose of this research is to search for halogenating agents coupled with PPh_3 to transform benzylic and allylic alcohols to their corresponding halides, especially chlorides and bromides in high yield under mild condition compared with related methods cited in previous literatures.

The chlorination of benzylic and allylic alcohols utilizing a combination of $\text{PPh}_3/\text{Cl}_3\text{CCONH}_2$ furnished the desired chlorides in good yield under mild condition within short reaction time. The reaction of benzylic alcohols using $\text{PPh}_3/\text{Cl}_3\text{CCONH}_2$, besides the target benzylic chlorides, benzylic phosphonium compounds were detected as another product. The formation of phosphonium salts occurred *via* the competitive reaction ($\text{S}_{\text{N}}1$) could be reduced by modifying the condition. Primary and secondary benzylic alcohols could be converted into the corresponding benzylic chlorides in high to quantitative yield with low yield of phosphonium compounds *via* $\text{S}_{\text{N}}2$ displacement. Secondary benzylic alcohols bearing electron-withdrawing group at benzylic position appeared to be effective alcohols for transformation to chlorides without other by-products. For allylic alcohols, the desired chlorides were attained in good yield of largely unrearranged allylic chlorides except for terminal allylic alcohols. Secondary terminal allylic alcohols proceeded the desired chlorides *via* $\text{S}_{\text{N}}2$ mechanism, whereas tertiary terminal allylic alcohols generated an olefinic product *via* E_2 elimination in place of $\text{S}_{\text{N}}2$.

The bromination of benzylic and allylic alcohols utilizing a combination of $\text{PPh}_3/\text{Br}_3\text{CCO}_2\text{Et}$ or $\text{PPh}_3/\text{Br}_3\text{CCOCBr}_3$ could be smoothly converted to the desired bromides in high yield under mild condition within short reaction time. Primary and secondary benzylic and allylic alcohols appeared to be great reactive substrates yielding the corresponding bromides *via* $\text{S}_{\text{N}}2$ mechanism. Secondary and tertiary

allylic alcohols provided the rearranged product *via* S_N2' much more than an olefinic product occurred *via* E_2 .

Allylic alcohols were more reactive with all combinative reagents using in this research than benzylic alcohols.

Proposal for the Further Work

This developed methodology can be used to prepare the desired halides in excellent yields with high regioselectivities. Therefore, the utilization of PPh_3 /brominating agent system may be extended to prepare conjugated dienes from the dehydration of tertiary alcohols. In addition, compound **B** which is the intermediate for the preparation of rapamycin may be synthesized by halogenation of allylic alcohol **A**.

