

Abstract

This thesis is presented in three parts.

In the first part, the ring expansion of 1-vinylcycloalkenols promoted by hydroxy(tosyloxy)iodobenzene (HTIB) is discussed. This study focused on the synthesis of seven-membered ring compounds. This reaction is versatile, because different ring expanded molecules could be obtained by slightly changing the reaction conditions. Furthermore, it was possible to synthesize an eleven-membered ring keto-lactone by oxidative cleavage in good yield, achieving a relatively complex structure in four steps.

In the second part, the iodine catalysed cyclization of homoallylic alcohols promoted by HTIB and iodobenzene diacetate (DIB) is investigated. This reaction allows to obtain tetrahydrofuran derivatives disfavored by Baldwin's rules. A mechanism was proposed based on intermediates isolated from the cyclization and in previous data from literature.

Finally, the last part describes the application of high-resolution electrospray mass spectrometry for the elucidation of the disproportionation reaction of DIB and of HTIB in acetonitrile. It is supposed that mechanism of formation of iodine(I) and iodine(V) from DIB involves dimeric intermediates like $[\text{PhI}(\text{OH})\text{OIPh}]^+$, $[\text{PhI}(\text{OAc})\text{OIPh}]^+$, $[\text{PhI}(\text{OAc})\text{OI}(\text{O})\text{Ph}]^+$ and $[\text{PhI}(\text{O})\text{OAc}]^+$. By the other hand, the main species involved in the disproportionation of HTIB, are the dimers $[\text{PhI}(\text{OH})\text{OIPh}]^+$, $[\text{PhIO}(\text{OTs})\text{IPh}]^+$ and $[\text{PhI}(\text{OTs})\text{OI}(\text{O})\text{Ph}]^+$.

Keywords: hypervalent iodine, ring expansion, cyclization, desproportionation, mass spectrometry.