

Abstract

The present Ph.D. thesis deals with the hetero-Diels-Alder (HDA) reactions of aromatic aldehydes with conjugated dienes catalyzed by Ti(IV) catalysts and other Lewis acids.

The first chapter incorporates a general review of the HDA reactions of the carbonyl compounds covering literature up to July 2015.

In the second chapter, the results of the theoretical and experimental investigation of the HDA reactions of the aromatic aldehydes with simple dienes in the absence and presence of the TiCl_4 as catalyst have been presented. It is found that in the absence of a catalyst, the activation enthalpies are very high, which come down remarkably in the presence of TiCl_4 . Guided by these theoretical results, we accomplished successfully the HDA reactions of six aromatic aldehydes in the presence of TiCl_4 . Structures of the products were duly confirmed on the basis of IR, ^1H NMR and ^{13}C NMR studies. Thus, we for the first time reported the HDA reactions of aromatic aldehydes with simple dienes in the presence of TiCl_4 as catalyst (Sogani et al. *Tetrahedron*, **2014**, *70*, 735).

In the third chapter, the results of the theoretical and experimental investigation of the asymmetric HDA reactions of the aromatic aldehydes catalyzed by ((*R*)-1,1'-bi-2-naphthoxy)titanium dichloride have been presented. The reactions occurred with good to high enantiomeric excess (68- 95% *ee*), as determined by high performance liquid chromatography (HPLC) method using chiral OJ-H column. The

results form the basis of our research paper accepted to Current Catalysis (Current Catalysis, 5(1), 2016).

The last chapter incorporates theoretical results of the catalytic activity of the Lewis acids, namely AlCl_3 , EtAlCl_2 , BF_3 and ZnCl_2 . The activation enthalpies are found to increase in the order, $\text{AlCl}_3 < \text{EtAlCl}_2 \approx \text{BF}_3 < \text{ZnCl}_2 \ll \text{uncatalyzed}$. Encouraged by these results, we carried out successfully the HDA reactions of aromatic aldehydes in the presence of EtAlCl_2 . All the products were duly characterized on the basis of IR, ^1H NMR and ^{13}C NMR studies.