Abstract

Chapter I: General introduction of carbon-heteroatom bonds

The backbone of many organic compounds is composed of C–C bonds, but the function of these molecules is often derived from the presence of heteroatoms, such as nitrogen, oxygen and sulphur, which are held in these molecules by C–heteroatom bonds. Although, C-heteroatom bond forming reactions is thermodynamically much more favourable than C-C cross coupling reactions, C-heteroatom bond formation has occupied unique site in organic chemistry. For example, most of the pharmaceuticals often contain C–N bonds and almost all natural products contain C–O bonds. Heterocyclic compounds in which C–N, C–O or C–S bonds are present in the ring structure are found in all applications of chemistry. Extensive work has been done on exploring the importance of C-hetero bond towards the biological, synthesis and designing new class of drugs and material properties associated with these classes of compounds. The huge importance and broad scope of carbon-hetero bond create a keenness to author to carry out the methodological work for carbon-heteroatom bond forming reactions.

Chapter-II: Selective epoxidation of steroidal skeleton by *m*-chloroperbenzoic acid (*m*CPBA)

Section –A: Chapter II (section-A) deals with methodical literature review on epoxide, its synthesis and *m*CPBA. Epoxide is considered as useful intermediate for the synthesis of wide range of compounds with biological interest. Epoxidation of olefins can be carried out with various catalytic systems. *m*CPBA is well known reagent for the epoxidation and rearrangement of various types of natural and synthetic substances. The detail literature survey reveals that there is still a requirement of easy, green and new protocols for the epoxidations.

Section – B: Chapter II (section-B) deals with the selective epoxidation of 16-dehydropregnenolone acetate (16-DPA) by m-chloroperbenzoic acid (*m*CPBA). The epoxidation of 16-DPA by *m*CPBA on activated silica at room temperature furnished only 5, 6-monoepoxy derivative but the same reaction in $CHCl_3$ under reflux condition offered 5, 6-16, 17-diepoxy derivative. The reaction on activated silica was extended to β-sitosterol, β-sitosterol acetate and β-sitosterol benzoate and found good result.

Chapter-III: Solid phase synthesis of oxime derivatives

Section –A: Chapter III (section-A) deals with methodical literature review on oxime, synthesis and its applications. Oximes are considered as a versatile organic intermediate for the synthesis of wide range of organic compounds. Classically, oximes were prepared by refluxing an alcoholic solution of a carbonyl compound with hydroxylamine hydrochloride and pyridine. The multiple drawbacks of classical method gave birth to the development of modern method for their preparation. The modern methods comprise the synthesis of oximes from diverse functional groups under varied reaction conditions. The need of new methodologies was come up due to various draw-backs of existing methodologies.

Section –B: Chapter III (section-B) deals with the selective oximation of carbonyl compounds by hydroxylamine hydrochloride on silica under solvent free conditions. The 1, 2 aromatic dicarbonyl compounds furnished exclusively monoxime at room temperature and dioxime at elevated temperature. The aromatic aldehydes, alicyclic carbonyl also offered excellent yield. The aromatic ketones furnished no yield at room temperature but offered excellent results at elevated temperature. No selectivity was found in alicyclic 1, 2 and 1, 3 dicarbonyl compounds.

Chapter-IV: $FeCl_3$ mediated one-pot transformation of aldehydes into nitriles

Section –A: Chapter IV (section-A) deals with methodical literature review on nitriles, synthesis and its applications. Nitriles are considered as important intermediate for the functional group transformation and heterocyclic synthesis. During the last decades, use of various catalytic systems has been established for the oxidative transformation of nitrile from various functional groups. The demand and need of new protocols were come up owing to various draw-backs of existing methodologies.

Section- B: Chapter IV (section-B) deals with the ferric chloride mediated one-pot transformation of aromatic aldehydes into nitriles. The reaction were carried out by adding aldehyde (1 mmol) and hydroxylamine hydrochloride (1.2 mmol) to a solution containing anhydrous ferric chloride (0.5 mmol) in 5 ml dry DMF. The excellent yields of desired products were obtained under reflux condition. All aromatic aldehydes furnished good to excellent yield except the aldehyde having electron withdrawing group which furnished comparatively lower yield.

Chapter-V: $MgCl_2.6H_2O$ catalyzed synthesis of 2-substituted benzimidazoles

Section –A: Chapter V (section-A) deals with methodical literature review on benzimidazoles, synthesis and its applications. Benzimidazole is an important substructure found in many pharmaceuticals. Numerous methodological works has been done to prevail over the draw-backs of classical methods. The comprehensive literature review reveals that there is still a need of straight forward method for the synthesis of benzimidazoles.

Section –B: Chapter V (section-B) deals with $MgCl_2.6H_2O$ catalyzed synthesis of 2-aryl or heteroaryl substituted benzimidazole derivatives from 1, 2-phenylenediamine and aryl or heteroaryl aldehydes. The reaction mixture was stirred on magnetic stirrer at 60 ^{o}C for appropriate time to furnish desired products. The aliphatic aldehydes do not provide any product. The poor reactivity of aliphatic aldehydes might be because of possible enolization of carbonyl.

Chapter-VI: Synthesis of substituted imidazoles on titanium incorporated silica solid support

Section –A: Chapter VI (section-A) deals with methodical literature review on imidazole, synthesis and its applications. Imidazole is regarded as important substructure found in many bioactive compounds. In view of the diverse applications associated with these derivatives, the development of more convenient synthetic protocol is highly encouraging. The detail literature review reveals that numerous protocols has been developed under varied catalytic system but there is still a paucity of green and cost efficient protocol for the synthesis of imidazole derivatives.

Section –B: Chapter VI (section-B) deals with the synthesis of tri- and tetra-substituted imidazole on titanium incorporated silica solid support under solvent free conditions. The synthesis were carried out by mixing titanium incorporated silica intimately with benzil/benzoin, aromatic or hetero-aromatic aldehydes and ammonium acetate under solvent free conditions. The desired products were obtained at 90 ^{o}C. The solid support was recycled and used up-to five consecutive reaction runs. The detail quantification of titanium on silica by electron diffraction X-ray spectroscopy before and after recycling suggested that no significant loss of titanium from silica. The solid support was found equally applicable for the synthesis of tetrasubstituted imidazoles.