CHAPTER 8

CHEMISTRY

Doctoral Theses

090. AGRAWAL (Arpita)
Novel Synthetic Methodologies Using Microwave, Nickel Boride and $MoO_5.H_2O$.HMPA Complex
Supervisor : Prof. J. M. Khurana
Th 15459

Abstract

Presents some novel synthetic methods, namely (i) microwave mediated stereoselective debromination of vicinal-dibromides supported on silica gel and acidic alumina inorganic solid supports to give olefinds, (ii) a two step synthesis of 3,4-dihydro-4-oxo-5H-pyrano(2,3-d)pyrimidines starting from chalcones and thiobarbituric acids, (iii) desulfurization of 5,5-diaryl and 5-alkyl-3-phenyl and 3-phenyl-2-thiohydantoins with nickel boride to give corresponding imidazolidones, and (iv) oxidation of sulphides, selenides and tellurides with $MoO_5.H_2O$.HMPA complex to the corresponding dioxides.

Contents

091. AMIT KUMAR
Theoretical Studies of Electronic Structures and Condu ction Properties of Electrically Conducting Copolymers
Supervisor : Prof. A. K. Bakhshi
Th 15251

Abstract

Studies systematically the electronic structures and conduction properties of both periodic and aperiodic $(A_mB_n)x$, $(B_mC_n)x$ and $(A_mC_n)x$ copolymers of three thiophene based donor-acceptor polymers abbreviated as PHTh (A)x, PFTh (B)x and PCNTh (C)x. Shows that the higher percentage of low band gap component in a copolymer chain improves its n-dopatphilicity while the higher percentage of large band-gap component, besides improving its p- dopantphilicity makes it a bettter intrinsic conductor of electricity. Investigate the effect of change of valence and conduction band widths of the homopolymers on the electronic structures and conduction properties of model copolymers of Type-I and Type-II staggered, respectively using Negative Factor Counting method in tight binding approximation. Shows that for both Type-I and Type-II stagered copolymers the trends in the electronic properties as a function of block sizes (m and n), composition (m/n) and the arrangement of units (periodic or aperiodic) remain same with change in the band widths of the homopolymers constituting the copolymer chain. Shows that the incorporation of vinylene linkages has a profound effect on the electronic properties of the donor-acceptor polymers and improves their conductivity both intrinsically as well as extrinsically. Further, it has been found that a regular alternation of vinylene units and units of donor-acceptor polymer in a copolymer chain is an efficient way for designing polymers with good prospects for both intrinsic and extrinsic conductivity.

Contents

092. ARJUN SINGH

AB-INITIO Study of Some Molecular Electronic Structures and Reaction Paths

Supervisors : Prof. R. C. Rastogi and Prof. N. K. Ray

Th 15252

Abstract

Observes that the inclusion of electron correlation significantly decreases the activation energy and makes the reaction less endothermic. Calculated ^{13}C NMR chemical shifts of uric acid are in good agreement with the available experimental results. Calculated energetics of keto-enol tautomerization are in good agreement with the results of high level ab-initio method. Concludes that the computationally economical B3LYP density functional with moderate size basis set(s) is quite adequate to study a variety of properties like potential energy surfaces, energetics, NMR chemical shifts and spin-spin coupling constants of the chemical systems.

Contents

093. BHATNAGAR (Pallav)

Structural and Functional Characterization of Single Nucleotide Polymorphisms (SNPs) in the G-Protein Coupled Receptor

Supervisor : Dr. Shrikant Kukreti

Th 15253

Abstract

Explains the biological role of two clinically relevant polymorphisms of one of the important member of the G-protein coupled receptor. The results supported by other evidences, highlights the importance of the hydrophobic parameter. It can be suggested that the biological explanation of the role played by change in hydrophobicity can be attributed to solvent accessibility related biological functions. In this study, these SNPs have failed to show any effect on the expression profile of the receptor.

However, the fact that in this study the Arg16Gly and Gln27Glu have no influence on gene expression, the rationale for the association of these polymorphisms with numerous diseases remained unanswered. Therefore, the post-translational biological events may be considered for unraveling the reason for the reported clinical associations. Available literature suggests that the post-translational modification may influence many of the physico-chemical and biological properties of the proteins, such as protein folding, stability, cellular trafficking etc. The change in the hydrophobicity alongwith the location of the Arg16Gly polymorphism within a conserved glycosylation site suggests the role of this polymorphism in cellular trafficking. This may cause decrease in the translocation of newly synthesized receptor from internal compartments to the cell surface.

Contents

1. Introduction and review of literature. 2. Molecular dynamics simulations of nona-peptides. 3. Synthesis, purification and characterization of nona-peptides. 4. Biophysical and biochemical analysis of nona-peptides and promotor region polymorphism. 5. Influence of single nucleotide polyorphisms (SNPs) on gene expression profile. 6. Results and conclusion and bibliography.

094. BRAJENDRA KUMAR SINGH
Synthesis of Novel Bioactive Thionylated Polyphenolics and Pyrazinone Derivatives using Microwave Irradiation under Solid Phase Conditions and Simultaneous Cooling
Supervisor : Prof. V. S. Parmar
Th 15254

Abstract

Synthesizes several oxygenated coumarins and corresponding thionocoumarins and have studied their inhibitory activities on TNF-α induced expression of ICAM-1 and on NADPH-catalysed liver microsomal lipid peroxidation for understanding the mechanisms underlying the anti-inflammatory activities of compounds of this class and for establishing structure-activity relationship. Investigates the influence of microwave irradiation on the Chan-Lam cross-coupling reaction to carry out the coupling at the N-1 position of the 2(1H)-pyrazinone scaffold via Cu(II)-mediated cross-coupling protocol. Also developed a new transition metal-catalyzed orthogonal solid-phase protocol, based on sequential Chan-Lam arylation and Liebeskind-Srogl cross-coupling reaction, for the decoration of the 2(1H)-pyrazinone

scaffold. The final compounds were released from the solid support applying a new "traceless linking" strategy, where the sulfur linker is cleaved without prior oxidation, resulting in the formation of a new C-C bond.

Contents

1. Synthesis of novel bioactive thionylated coumarins and esters. 2. Copper(II)- mediated cross-coupling of arylboronic acids and 2(1H)- pyrazinones facilitated by microwave irradiation with simultaneous cooling; synthesis of 2(1H)-pyrazinone derivatives on solid support and Summary.

095. CHANDAN KUMAR SINGH
Functionalised Macrocyclic Ligands, Synthesis, Characterization and Development of Electrochemical Sensors
Supervisor : Dr. Sulekh Chandra
Th 15457

Abstract

Six macrocyclic ligands have been synthesized, characterized thereafter and then used as metal ion selective PVC based membrane electrodes as electroactive materials. These macrocyclic compounds are highly sensitive and selective towards some specific transition and heavy metal ions. The electrodes developed have been analysed by testing some practical samples and using them as electrone indicator electrode.

Contents

1. Introduction 2. Methodology of ion selective electrodes. 3. Materials and instruments used and synthesis and characterization of macrocyclic ligands. 4. Development of Poly(Vinyl chloride) based Cr(III)-selective electrode using macrocyclic ligand L_1 as ionophpre; Development of Poly(Vinyl chloride) based Al(III)-selective electrode using macrycyclic ligand L_2 as ionophpre and Development of Poly(Vinyl chloride) based Co(II)-selective electrode using macrocyclic ligand L_3 as ionophpre. 5. Development of Poly(Vinyl chloride) based Cu (II)-selective electrode using macrocyclic ligand L_3 as ionophpre; Development of Poly(Vinyl chloride) based Th (IV)-selective electrode using macrocyclic ligand L_3 as ionophpre and Development of Poly(Vinyl chloride) based Pb(II)-selective electrode using macrocyclic ligand L_6 as ionophpre.

096. CHAUHAN (Sushila)
Synthesis and Characterization of Copolymer of Polylactamide and Amino Acid with Silicon as Binder
Supervisor : Dr. Man Singh
Th 15255

Abstract

Prepares and utilizes polymeric moieties and biomolecules with semiconductor, silicon as discrete molecular building blocks in versatile supramolecular assemblies. Silicon based conductive biocompatible copolymers have been synthesized using the basic experimental techniques. PVP, a biocompatible polymer and alpha amino acids basically glycine 1-alanine and 1-leucine are chosen for the copolymer synthesis. Silicon a semiconductor is introduced as bridge in the copolymers for binding the two polymeric species. Silicon taken in the form of tetraethylorthosilicate is converted into silicic acid via sol-gel technique. Characterization was made using the spectrophotometric measurements basically IR, NMR etc., and thermogravimetric measurements and supported by CHN and physicochemical measurements.

Contents

097. DUA (Amita)
Conformers and Metal Complexes of Thiohydroxamic Acids : A DFT Study
Supervisor : Prof. Rita Kakkar
Th 15456

Abstract

Studies thiohydroxamic acids, with an idea to better understand their structures and bonding behaviour. Thiohydroxamic acids [RC(=S)NR'OH] (N-hydroxythioamides), like their hydroxamic acid counterparts, play important roles in analytical and biological chemistry. This interesting class of compounds contains the four-atom unit of diverse atoms C_{sp2}, S, N and O. The presence of three electronegative atoms, S, N and O, ensures that they have interesting properties as powerful bidentate ligand, utilizing the S and O atoms, and have found applications in analytical determination of several metals, as well as being used in na-

ture for the transport of many metal ions. O-acyl derivatives of thiohydroxamic acids are efficient precursors of C, S, N, or P radicals.

Contents

1. Introduction 2. Computational methods. 3. Structures of thiohydroxamic acid tautomers. 4. Barriers to intramolecular rearrangements. 5. Infrared spectral studies of N-(p-ethylphenyl)thiobenzohydroxamic acid. 6. Metal ion complexes of thioformin. 7. Conclusions and perspectives.

098. JITENDRA KUMAR

Poly(3-Octylthiophene) : Synthesis, Characterization and Applications in Memory Devices and Solar Cells

Supervisors : Prof. R. C. Rastogi and Dr. Ramadhar Singh

Th 15256

Abstract

π-Conjugated polymers (CPs) are a new source of materials for developing low cost electronic devices in place of inorganic semiconducting (ISC) materials. There are many advantages of CPs over ISCs such as easy molecular architecting, huge scope of property control by changing synthetic and processing parameters, compatibility with other materials to form composites, environmental stability, light weight, device architectural flexibility, and above all, the low cost of end product makes them the most fascinating electronic materials for developing various electronic devices. Understands semiconducting organic polymer, a π-conjugated polymer, from the point of view of optimal synthesis and processing parameters, variables that affect supramolecular assesmbly of π-conjugated polymeric chains at nanoscopic to microscopic scale, charge generation (doping) and its transport, and finally, its utilities in electronic devices.

Contents

1. Introduction and conducting polymers. 2. Soluble poly (3-Alkylthiophene)S : Synthesis and processing methodoligies. 3. Supramolecular assemblies of poly (3-octylthiophene). 4. Structure-morphology-DC conductivity correlation in ferric chloride doped poly(3-octylthiophene). 5. AC conductivity and dielectric relaxation in poly (3-octylthiophene). 6. Memory and solar devices based on poly (3-octylthiophene).

099. KHURANA (Shilpi)
Design and Synthesis of Novel Natural and Unnatural Compounds of Biological Importance and Phytochemical Investigation of Aerial Roots of Ficus Religiosa.
Supervisor : Prof. S. C. Jain
Th 15257

Abstract

Marine derived drugs are present in very small amounts in the natural source and simply harvesting the source organism and extracting the active chemical does not look to be a viable option, the study therefore developed a general and convenient method, not only for their synthesis but also for their derivatives, in order to confirm the assigned constitution to the natural products and to obtain them in sufficient amounts for broad spectrum bio- analysis. In view of the various biological activities of the C_{13} anacardic acid (13:0) and its cis monoenoic (13:1) memeber, isolated from outer green shells from pistachio nut, pistachia vera, undertook the synthesis of 6-[8'(Z) ,11'(Z)-tridecadienyl] salicylic acid by introducing an additional double bond at C_{11} position along with some other biologically active analogues. For their synthesis, the study developed a new and convenient method starting from methy 1-6 bromomethyl -2 methoxybenzoate as a potent intermediate.

Contents

100. KUKREJA (Shuchi)
Eco-Friendly Synthetic Approaches for Bioactive Compounds.
Supervisor : Prof. M. Kidwai
Th 15258

Abstract

Isoxazoles and pyrazolines are useful structural moieties in medicinal chemical because of their close association with various biological activities. Compounds containing isoxazole nucleus have been reported to possess antimicrobial,

antitumour, antiulcer, anti-inflammatory, anti-hypertensive, spermicidal and bactericidal activities. Whereas pyrazolines have been shown to have antifungal, antiviral, antibacterial and analgesic activities. In view of biological importance of these compounds, their synthesis via a green method using anhydrous K_2CO_3 as a solid support under microwaves to afford isoxazoles and pyrazolines respectively. Designed a single step protocol for regioselective synthesis of 1,2,4-triazepine using molecular iodine as a novel catalyst. Developed a protocol for ambient synthesis of 1,4-dihydropyridines using recyclable Cupric sulfate pentahydrate, a mild lewis acid as a novel catalyst.

Contents

101. MOTHSRA (Poonam)
Chemical and Biochemical Studies in Heterocycles
Supervisor : Prof. M. Kidwai
Th 15458

Abstract

Synthesis of pharmacologically important compounds, a simple and efficient synthesis of 2,4,5-trisubstituted imidazoles and 1,2,4,5-tetrasubstituted imidazoles have been developed. The diverse therapeutic activities of hydrazones and 1,2,4-triazines and the advantages of coupling neat synthesis with microwave, various derivatives have been synthesized. Explores the synergism of enzymes under microwave. L-Ascorbyl fatty acid esters, which are very important antioxidants. Commercially available enzyme CAL-B is also studied under microwave during the acylation of bioactive 7-Hydroxy-4-methylcoumarine. 1,5-Benzodiazepines and their derivatives have been investigated extensively by organic chemists due to their close association with biological activities.

Contents

1. 1-Aryl-4,6-Diamino-1,2-Dihydrotriazine as antimalarial agent : A new synthetic route. 2. Iodine catalyzed synthesis of highly substituted imidazoles from Benzil. 3. Elemental iodine catalyzed one-pot synthesis of 2,4,5-trisubstituted imidazoles from benzoin and One-pot synthesis of 1,2,4,5-tetrasubstituted imidazoles from benzoin using catalytic amount of iodine. 4. Neat synthesis for the library of antimalarial compounds. 5. Green enzymatic synthesis of L-ascorbyl fatty acid esters and Enzyme catalyzed acylation of 7-hydroxy-4-methyl-2H-chromene-2-one using microwave. 6. Neat reaction technology for the synthesis of novel 1,5-benzodiazepines and Microwave assisted neat synthesis of thiadiazine library and Summary.

102. PRATIBHA KUMARI

Biomimetic oxidation and Related Reactions with Metallomacrocycles

Supervisor : Prof. S. M. S. Chauhan

Th 15259

Abstract

Metalloporphyrins have been used as chemical models of cytochrome P450 to mimic oxidative metabolism of xenobiotics including herbicides with different monooxygen donors. Several reductive metabolites such as flavan-4-α-ol, trans-3-hydroxyflavan-4-β-ol and 6-hydroxyflavan-4-β-ol, apart from oxidized metabolites have been reported in the metabolism of flavonoids in mammals. The reduction of 4'-methoxyflavone with sodium borohydride catalyzed by cobalt(II) phthalocyanines gave 4'-methoxyflavan-4-ol in methanol at room temperature under nitrogen atmosphere. The structure of the product was confirmed by ^{1}H NMR, IR and ESI-MS spectroscopic data. The e ffects of changing molar ratio between substrate, sodium borohydride and cobalt(II) phthalocyanine catalyst have been examined. The edge-to-face-assembly via metal-nitrogen coordination involving the pyridyl nitrogen atom of one molecule and the metal ion of a second molecule in zinc(II) 2(3), 9(10), 16(17)-trimethyltribenzo(b.g.l)pyridino(3,4,q) porphyrazine has been studied by spectrofluorometry, UV-visible spectroscopy and electrospray mass spectrometry (ESI-MS).

Contents

1. Synthesis of metalloporphyrins and their use in the oxida-

tion of metribuzin and related compounds. 2. Synthesis of metallocorroles and their use in the oxidation of selected hydrocarbons. 3. Synthesis of metallophthalocyanines in ionic liquids and their application in the oxidation of flavones. 4. Synthesis and chemical studies of unsymmetrical phthalocyanines. 5. Synthesis of water soluble calix(n)arenes and their ionic interactions.

103. RAJIV KUMAR

Doped Inorganic Nanoparticles : Preparation, Characterization and Applications

Supervisors : Prof. N. K. Kaushik and Prof. Amarnath Maitra

Th 15260

Abstract

Several methodologies have been adopted for the preparation of fine ceramic particles like Sol-Gel, Co-precipitation, Spray dry methods, etc. but these methods suffer from inherent drawbacks of producing particles with larger dimensions and a broad polydispersity. To overcome these disadvantages different types of nanoparticles of inorganic materials (gold and silica) doped with biomolecules and active imaging agents, have been prepared within the controlled dimensions of the micellar core and reported in this work. Explores the possibilities of preparing core-shell nanoparticles which has been processed to make them hollow by leaching out the core. The aqueous core of the water in oil microemulsion was used as nanoreactor for the formation of nanoparticles. The size of the reverse micellar droplets of the water in oil microemulsion is in nanometer range, so the particles formed in the aqueous core are also in the same scale. Moreover, the conformation and activity of the biomolecules like enzymes depends upon the size of the host aqueous core. Therefore by tuning the size of the host aqueous core, biomolelcules of varying activities can be immobilized. Such doped nanoparticles can have potential applications in many frontiers, including sensors, biosensors, electrochemistry, immunochemistry, drug delivery, enzyme therapy, gene therapy etc.

Contents

nanoparticles : A novel carrier for enzyme therapy. 6. Fluorine (^{19}F) doped ormosil nanoparticles : A potential agent for magnetic resonance and optical imaging. 7. Conclusion.

104. RAJOR (Hament Kumar)
Chemical Speciation, Molecular Modeling and Antioxidant Activity Studies on Polyhydroxyphenols and Their Metal Complexes
Supervisor : Dr. R. K. Sharma
Th 15455

Abstract

Studies the complexation behaviour of three flavonoids; quercetin, morin and chrysin with the aim to correlate chelation or complexation ability with their antioxidant action. Antioxidant activities of flavonoids alone and their metal complexes have also been investigated. The mode of coordination in these ligands, lanthanide complexes are synthesized and characterized by using various analytical techniques, viz. elemental analysis, ^{1}HNMR, IR, UV-Visible and thermal analysis.

Contents

1. Introduction 2. Materials and theory of methods used. 3. Chemical speciation, molecular modeling and antioxidant studies on quercetin and its metal complexes. 4. Chemical speciation, molecular modeling and antioxidant studies on morin and its metal complexes. 5. Chemical speciation, molecular modeling and antioxidant studies on chrysin and its metal complexes. 6. Synthesis and characterization of Pr^{3}, Nd^{3+} and Sm^{3+} complexes of quercetin, morin and chrysin.

105. RAMANANDA SINGH (Mayanglambam)
Corrosion Inhibition of Mild Steel by Some Organic Compounds in Acid Medium
Supervisor : Prof. Gurmeet Singh
Th 15261

Abstract

Ascertains the role of some organic compounds as inhibitors during anodic dissolution of mild steel including metal dissolution and cathodic reduction of oxygen and hydrogen. The corrosion of mild steel in 1N sulphuric acid has been studied in the presence of Tetrabutylammonium bromide (TBAB), Triethano-

lamine (TEA) and Diethanolamine (DEA) in the present work. The methods used for study are galvanostatic polarization studies, impedance measurements, potentiostatic polarization studies, infrared spectroscopy, scanning microscopy and quantum chemical calculation. Many corrosion parameters have been calculated to interpret the results.

Contents

106. SAKHUJA (Rajeev)

Studies on Catalytic Activity of Azaphenothiazines and Synthesis of Novel Nitrogen Heterocycles of Biological Importance and Phytochemical Investigation of Tabebuia Palmeri

Supervisor : Prof. S. C. Jain

Th 15262

Abstract

Presents a synthetic methodology for the development of new class of anticancer agents involving azaphenothiazine nucleus. The biodynamic properties possessed by phthalimide nucleus, urged to investigate the biological potential of this heterocyclic system also by coupling it with the 1-azaphenothiazine moiety at the 10^{th} position, with the help of an alkyl linker. Develops a more convenient and efficient method for the synthesis of such biologically potent 10-{n-(phthalimidoalkyl)} pyrido(3,2-b)(1,4)benzothiazines under microwave irradiation. Successfully synthesized these by reacting 1-azaphenothiazines with different N-(bromoalkyl)phthalimides in presence of anhydrous K_2CO_3 using tetrabutylammonium bromide (TBAB) as a catalyst under microwave irradiation.

Contents

3,2'-thiazolidine)-2,4'-diones. 4. Phytochemical investigation of tabebuia palmeri and Summary.

107. SEEMA

Studies on the Characterization and Establishment of Human Placental Acetoxy Drug : Protein Transacetylase as Calreticulin Transacetylase

Supervisors : Prof. R. C. Rastogi and Prof. H. G. Raj

Th 15460

Abstract

Emphasizes that the characterization of TAase as CRT is expected to throw light on the newer physiological roles of this unique protein. Also, our investigations describe CRT for the first time as the enzyme (CRTAase) mediating the protein acetylation independent of acetyl CoA, and in biological systems Acetyl CoA is the substrate for CRTAase mediated protein acetylation. The studies reported also purport the role of PA as versatile donors of acetyl groups for CRTAase.

Contents

1. Isolation, purification and characterization of acetoxy drug : Protein transacetylase from human placenta. 2. Establishment of acetoxy drug : Protein transacetylase as calreticulin transacetylase. 3. Calreticulin transacetylase mediated acetylation of neuronal nitric oxide synthase (nNOS). 4. Molecular cloning, expression and purification of calreticulin transacetylase. 5. What is the physiological substrate for calreticulin transacetylase in biological system?

108. SHARMA (Himani)

Synthesis, Properties and Surface Modifications of Organically Capped CdSe Quantum Dots

Supervisors : Prof. Gurmeet Singh and Dr. S. M. Shivaprasad

Th 15263

Abstract

The emergence of colloidal semiconductor nanocrystals have generated great fundamental and technical interest in recent years, and represent one of the most rapidly developing areas of current semiconductor research. The size dependent emission property for Cadmium Selenide (CdSe) quantum dots renders it indispensable in the field of nanocrystal-based emitters such

as light-emitting diodes, photovoltaic devices, lasers, biomedical tages, etc. For this reason, the control of the photoluminescence (PL) properties by controlling the size of the semiconductor nanocrystals has been a major goal in the synthesis of colloidal semiconductor nanocrystals. Investigation of these semiconductor quantum dots reveals the evolution of the electronic structure from an extended solid state to the molecular limit, an extremely important issue of basic and applied research in condensed matter physics. The work presented in this thesis mainly deals with the synthesis and characterization of the CdSe nanoparticles. The growth of nanostructured CdSe prepared by novel methods have been experimentally investigated and the confinement, stability and surface modifications aspects of the quantum dots are studied.

Contents

1. Introduction 2. Experimental techniques. 3. Synthesis and characterization of CdSe quantum dots. 4. Aspect of quantum confinement and stability issues in CdSe quantum dots. 5. Surface modifications of CdSe quantum dots : Role of organic and inorganic groups. 6. Studies of polymer-CdSe nanocomposites.

109. SHARMA (Vandana)
Novel Redox Methods in Organic Synthesis and Inhibition Studies of Urease
Supervisor : Prof. J. M. Khurana
Th 15264

Abstract

Discovery and applications of new reagents and reactions has always been the most facinating aspect of synthetic organic chemistry. Synthetic methodology offers a great challenge for organic chemists. The emphasis is always on selectivity, high yield of products, easy availability of reagents, mild reaction conditions and easy work up of the reactions. Development of new reagents or exploring newer useful synthetic applications of some versatile reagents in an integral part of development of synthetic methodology. Therefore, the search for new efficient, readily available and inexpensive reagents, milder reaction conditions to bring about some unique transformations and devise novel protocols for the synthesis of pharmaceutically important heterocyclic compound continues. Further, novel heterocyclic compounds provide a wide application in the arena of enzyme inhibition which is an important area of pharma-

ceutical research since studies in this field have already led to the discovery of wide variety of drugs useful in a number of diseases. Specific inhibitors interact with enzyme and block their activity towards their corresponding natural substrates. Both reversible and irreversible inhibition is useful. The importance of enzyme inhibitors as drugs is enormous. Thus there is need for searching and tailor designing new molecules which show effective inhibition and can be employed for treating a number of physiological conditions.

Contents

1. Deoxygenation of sulfoxides, selenoxides, telluroxides, sulfones, selenones and tellurones with magnesium-methanol. 2. Desulfurization of 2-substituted 3-thioxo-2-H-imidazo-(1,5-b)isoquinoline-1,5-diones with nickel boride. 3. Review on urease structure, mechanism and inhibition. 4. Standardisation of urease assay by indophenol. 5. Inhibition studies of urease by substrate based analogues. 6. Inhibition studies of urease by zymogram. 7. Experimental. 8. Summary and conclusions.

110. SINGHAL (Kavita)
Synthetic Strategies for Heterocyclic Compounds
Supervisor : Prof. M. Kidwai
Th 15264

Abstract

Pyrimidines and its pyrrolo fused derivatives have been studied for over a century due to their wide pharmaceutical applications as antimicrobial, antitumor, antihypertensive and anti-inflammatory agents and also possess significant inhibitory activity against various enzymes. The solid support, montmorillonite K-10 clay is a class of inexpensive and non-corrosive solid acids and has reached great development when combined with microwave irradiation (MWI) in different areas of organic synthesis due to their environmental compatibility. Thus, the synthesis of pyrrolo)2,3-d)pyrimidines exploring the Paal Knorr reaction was performed. In view of the growing importance of microwave (MW) in organic synthesis, it was thought worthwhile to extend this technology to carry out the reaction of chalcones of N,N-disubstituted thiobarbituric acids, amines with nitromethane under MWI to synthesize pyrrolo(2,3-d) pyrimidines. Increasing evidence suggests that electron-rich nitrogen heterocyclic compounds play an important role in diverse pharmacological activities. Introduction of a pyrazolidine ring in place

of the β-lactam ring resulted in enhanced activity and hence widely used in drug chemistry. In recent times, room temperature ionic liquids have attracted increasing interest in the area of green chemistry. In an endeavor to develop a green protocol and the biological activities of pyrazolines, a facile and rapid synthesis of pyrazolines using basic ionic liquid is reported.

Contents

111. VINEET KUMAR

Strategies Towards Selective Benzoylation of Nucleosides and Development of Novel Carbohydrate Based Chiral Ionic Liquids

Supervisor : Prof. V. S. Parmar

Th 15266

Abstract

Carries out benzoylation reactions on nucleosides of both ribo and deoxyribo series using benzoyl cyanide as benzoylating reagent, DMAP as catalayst and the ionic liquid 1-methoxyethyl-3-methylimidazolium methanesulfonate [(MoeMIM)(Ms)] as the reaction medium. All the nucleosides were found to be highly soluble in this ionic liquid. In all the cases, benzoylation occurred selectively and/or preferentially on the -OH groups of nucleosides over the $-NH_2$ group. The ionic liquid (MoeMIM)(Ms) was recovered easily after the reaction and reused upto 3 times without the loss of selectivity and yield. Synthesized a series of mono-ammonium and bis-ammonium chiral ionic liquids using isomannide as the starting material, which is commercially available and can be obtained by double dehydration of mannitol (one of the major byproducts in starch industries). The isoamannide was first treated with tosyl chloride in basic conditions to give its mono-tosylate (major) and di-tosylate (minor). The free hydroxyl group of mono-tosylate was then convered to its ethyl either derivative and tosylate group was then substituted by sec-amine using benzylamine, which was then quarternized to tetra-ammonium iodide salt using CH_3I/K_2CO_3.

This iodide salt on anion metatheisis afforded corresponding CILs. Similar approach was followed to obtain the bis(ammonium) CILs starting from ditosyl-isomannide. The applications of these novel CILs in chiral recognition, as chiral shift reagents in NMR spectroscopy and in determination of ee value have been studied by analyzing their diasteromeric interaction with racemic and (S)-Mosher's carboxylate using ^{19}F NMR spectroscopy.

Contents

1. Benzoylation of nucleosides in ionic liquid (MoeMIM)(Ms) using benzoyl cyanide as benzoylation reagent. 2. Synthesis and applications of carbohydrate based chiral ionic liquids and Summary.

M.Phil Dissertation

112. ARORA (Preeti)
Synthesis and Characterization of Novel Amino Flavones as Potential Anticancer Agents
Supervisor : Dr. Satish K. Awasthi