

2012 WNYACS Undergraduate Research Symposium



The Fifth Annual
Undergraduate Research Symposium

Sponsored by the Western New York Section
of the American Chemical Society

Saturday April 14, 2012

Canisius College, Buffalo, NY



Welcome Message From The Organizing Committee

Welcome to the 5th annual Undergraduate Research Symposium sponsored by the Western New York Section of the American Chemical Society. During these 5 years, our Symposium has evolved into a valuable experience for area students and an inspiration to research mentors. A strength of the WNY local section's Undergraduate Research Symposium is our ability to cross regional and international boundaries to increase appreciation for our students' work. This event's organizers have developed a tradition of collaboration that helps make the event successful and promotes professional contacts among the colleges and universities of western New York and southern Ontario.

Thanks go to our presenters and especially to our keynote speaker, Todd Krauss, Ph.D. of the University of Rochester. I would also like to extend my appreciation to the volunteers from the Canisius College Student Chapter of the ACS, to the members of the Organizing Committee and to our generous sponsors.

Sincerely,
Timothy Gregg, Ph.D.
Chair, 2012 Symposium Committee

2012 Symposium Organizing Committee

Chair: Dr. Timothy M. Gregg
Department of Chemistry and Biochemistry, Canisius College

Dr. Sarah E. Evans
Department of Chemistry and Biochemistry, Canisius College

Dr. Sarbajit Banerjee
Department of Chemistry, University at Buffalo, SUNY

Dr. Valerie A. Frerichs
Department of Chemistry, University at Buffalo, SUNY

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Canisius College**

Our Keynote Speaker



Dr. Todd D. Krauss received his B.S., M.S., and Ph.D. in Applied Physics all from Cornell University, completing his Ph.D. under the direction of Frank Wise. Upon graduation in 1998, he moved to Columbia University, serving as a postdoctoral fellow with Louis Brus until 2000, when he joined the Chemistry faculty at the University of Rochester.

Dr. Krauss is currently Professor of Chemistry in the Department of Chemistry and in the Institute of Optics at the University of Rochester. He is also the director of the Nano and Optical Materials Chemistry Cluster. His research interests involve fundamental studies of materials at the nanometer scale, their use in renewable energy and biotechnology, and the applications for nanometer scale materials in the areas of novel biological sensors, efficient and inexpensive solar cells, and nano-optical devices.

Current investigations in Dr. Krauss's lab are focused on fundamental studies of carbon nanotubes and semiconductor nanocrystals, and the integration of these materials into both novel non-linear optical devices and biological sensors. These studies are highly interdisciplinary, and lie at the interface between chemistry, physics, applied physics, and materials science.

Schedule of Events

April 14, 2012

Montante Cultural Center

Canisius College, Buffalo, NY

- | | |
|------------------|---|
| 8:30 - 9:50 am | Registration/ Poster Setup |
| 9:50 - 10:00 am | Introductory Remarks |
| 10:00 - 11:00 am | Keynote Presentation by Dr. Todd D. Krauss,
Department of Chemistry, University of Rochester |
| | <i>Nanoscience and Nanotechnology: Where Size Really Does Matter</i> |
| 11:00 - 12:20 pm | Student Presentations |
| 12:20 - 1:30 pm | Lunch |
| 1:30 - 3:00 pm | Student Poster Presentations |
| 3:00 pm | Awards and Closing Remarks |

Oral Presentations

Time 10:00 AM - 12:15 PM

Keynote Address

1. 10:00 am **Todd D. Krauss** University of Rochester
Nanoscience and Nanotechnology: Where Size Really Does Matter

Student Presentations

2. 11:00 am **Nicholas D. Cultrara** University at Buffalo, SUNY
Non-hydrolytic Sol Gel Synthesis of HfO₂ Nanorods
3. 11:20 am **David Samuel** St. Bonaventure University
*Reactivity of the Vitamin B₆ Ring:
Identification of Singlet Oxygen Adducts and Intermediates*
4. 11:40 am **Nicholas T. Jacob** University of Rochester
*Efficient Methodology to Afford Structurally Diverse
Macrocyclic Organo-Peptide Hybrids (MOrPHs)*
5. 12:00 pm **L. Alanna Nash** Brock University
*The Directed Evolution of Trypsin
for Mediated Sol-Gel Processing of TEOS*

Oral Presentations

Talk 2

**Non-hydrolytic Sol Gel Synthesis of HfO₂
Nanorods**

*Nicholas D. Cultrara, Sean W. Depner, Sarbajit Banerjee**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Interest in HfO₂ (hafnia) nanomaterials has escalated because of the possible uses in high k-gate dielectrics, ceramics, high refractive materials, and ferroelastic materials. A non-hydrolytic sol gel process can be used to synthesize HfO₂ nanocrystals through a SN1 condensation process between a hafnium alkoxide and hafnium halide. Control over the length of these particles has been achieved through the sterics of the alkoxide precursor and via the periodic additions of hafnium alkoxide precursors during the course of the reaction. This approach allows the length to be tuned without a substantial change in the widths of the nanocrystals. These particles exhibit twin planes which are indicative of a Martensitic phase transformation between high-symmetry tetragonal and low-symmetry monoclinic phases. These twin planes occur during the transition from high to low symmetry to alleviate shear stress in the crystal structure. The monoclinic hafnia nanorods exhibit periodic organization of these twin defects, which is evidence of possible ferroelastic behavior. These particles are characterized using powder X-ray diffraction, high-resolution transmission electron microscopy (HRTEM) and dark-field HRTEM.

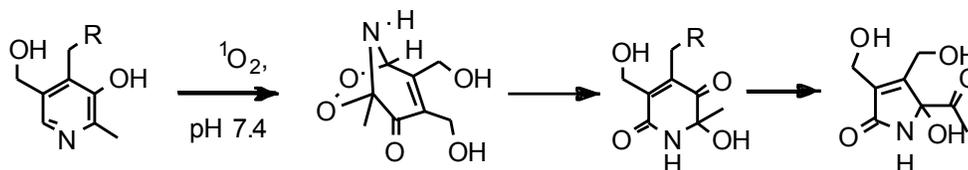
Talk 3

Reactivity of the Vitamin B₆ Ring: Identification of Singlet Oxygen Adducts and Intermediates

*David Samuel, Kirsten Norrell, Mark Ghassibi and David Hilmey**

Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY

Vitamin B₆ is a group of interconvertible vitamers that are versatile cofactors in biological systems. Recently, vitamin B₆ was also shown to have a secondary, protective effect against singlet oxygen. As an antioxidant, it quenches cellular reactive oxygen species that have been implicated in neurodegeneration and aging. Although vitamin B₆ is well defined as a cofactor, its antioxidant mechanism still remains poorly understood. In a series of time-course NMR experiments, we observed novel intermediates and products of B₆ oxidation. Using the photosensitizer Rose Bengal, we generated singlet oxygen to replicate pyridoxine-dependent quenching in phosphate buffered solutions. 1D and 2D NMR show the formation of two stable intermediates and a well-characterized, isolatable product. A low temperature study of the same reaction in methanol also revealed an unstable bicyclic endoperoxide intermediate that converted to a 2,5-dipyridone upon warming. The oxidation of other B₆ vitamers; pyridoxal, pyridoxamine, and pyridoxal-5-phosphate were similarly characterized in aqueous buffer by NMR directly from reaction mixtures. Compared to other 3-hydroxypyridines, these oxidations appear to be unique to the B₆ vitamer family. The oxidation mechanisms of pyridoxine and other B₆ vitamers will be discussed.



Talk 4

Efficient Methodology to Afford Structurally Diverse Macrocyclic Organo-Peptide Hybrids (MOrPHs)

*Nicholas T. Jacob, John R. Frost and Rudi Fasan**

Department of Chemistry, University of Rochester, Rochester, NY

Peptide-containing macrocyclic ligands have shown considerable promise towards modulating challenging biomolecular interactions, which makes them attractive molecular scaffolds as probes and potential pharmacological agents. Here we report a rapid and efficient methodology to afford conformationally constrained Macrocyclic Organo-Peptidic Hybrids (MOrPHs) via a tandem chemoselective reaction between a genetically encoded polypeptide and a bifunctional synthetic moiety. This strategy provides the opportunity to exploit both biosynthetic and synthetic combinatorial tools to generate relevant chemical diversity. The presented approach exploits a catalyst-free tandem reaction between a oxyamino/amino-thiol synthetic precursor and a genetically encoded intein fusion protein precursor incorporating a keto group. We will describe how this versatile methodology allows for the creation of diverse macrocycles of variable ring size, architecture, and amino acid composition by exploiting structurally different synthetic precursors as well as by varying the nature of the genetically encoded precursor.

Talk 5

The Directed Evolution of Trypsin for Mediated Sol-Gel Processing of TEOS

*L. Alanna Nash, P. Zelisko**

Department of Chemistry, Brock University, St. Catharines, ON

As society becomes more cognizant of the negative impact that we are having on our environment, there is a driving force to develop 'green' methodologies in chemistry in areas such as silica production where there is a heavy use of volatile compounds. Through the conjunction of rational design and directed evolution, an enhanced biocatalyst, trypsin, will be created to catalyze the production of silica. In order to evolve trypsin, initial experiments were taken to perfect the procedure for sol-gel processing.

Enzyme standards which consisted of trypsin, pepsin, papain papaya latex, papain carica papaya, and α -chymotrypsin were tested for their ability to hydrolyse tetraethoxysilane (TEOS), over a period of five hours. Both papain standards were capable at producing increased quantities of silicic acid over distilled water, with papaya latex papain well out performing the rest. Trypsin, pepsin and α -chymotrypsin standards were comparable to distilled water as a catalyst. This data shows that the majority of the enzyme standards are no better than water at catalyzing the hydrolysis of tetraethoxysilane, thus leaving vast room for improvement.

Lysates and whole cells of *E. coli*, *A. faecalis*, and *M. luteus* were also tested for the ability to hydrolyse tetraethoxysilane. Cells were lysed under both heating and freezing conditions, and allowed to hydrolyse tetraethoxysilane over 24 hours. The molybdenum blue assay tested for the presence of silicic acid. *E. coli* and *A. faecalis* lysates (frozen and heated) out competed whole cells, while *M. luteus*' whole cells produced higher quantities of silicic acid compared to its lysates.

- Poster 10.** **Aashish Abraham**, David Samuel and David G. Hilmey*
St. Bonaventure University, St. Bonaventure, NY
An Investigation of the Structural Requirements for the Antioxidant Activity of Vitamin B₆ through Pyridoxine Analogs
- Poster 11.** **Marie E. Albano, Chelsea L. Recor**, Megan McGahan and Ronny Priefer*
Niagara University, Niagara University, NY
Synthesis and multilayering of novel pseudo-polyelectrolytes into thin films
- Poster 12.** **Russell F. Algera, David J. Fortman** and Timothy M. Gregg*
Canisius College, Buffalo, NY
Cyclopropanation-cross-coupling strategy for synthesis of chiral alkylidene cyclopropanes
- Poster 13.** **Allen K Bourdon**, Luis A. Colon, Cody Vinci*, Ivonne M Ferrer, Lisandra Santiago, Amber Moore, Chi Man Ng, Sowjanya Garapati, Zuchin Xue, Jazmine Holmes, Erika Salem, Brian Tobahzinski and Nathan Guterry
University at Buffalo, SUNY, Buffalo, NY
Chromatographic Separation of Graphene Oxide Nanomaterial
- Poster 14.** **Marshall K. L. Binns, Justin P. Young** and Phillip M. Sheridan*
Canisius College, Buffalo, NY
Fourier Transform Microwave Spectroscopy of Alkali Metal Hydrosulfides: Detection of KSH
- Poster 15.** **Ankita Dubey**, Nicholas A. D. Burke and Harald D. H. Stöver*
McMaster University, Hamilton, ON
Synthesis and characterization of polyampholytes for use in cell-encapsulation
- Poster 16.** **Shannon Hritz**, Adam Townley, Nathalie VanderRijst, Hillary Chartrand, Melissa Rosenburg, Scott Macbeth, Yoon-Kook Kim, and Karen E. Torraca*
Houghton College, Houghton, NY
Palladium Catalyzed Reactions: A Search For A Greener Oxidation Pathway
- Poster 17.** **Amy L. Tran**¹, Kazushige Yokoyama^{1*} and Ronny Priefer²
¹*SUNY Geneseo, Geneseo NY*; ²*Niagara University, Niagara University, NY*
Self-assembly of Amyloid Beta Peptide Over Dialkoxy Disulfide Functionalized Nano Gold Colloidal Particles
- Poster 18.** **Steven M. Henderson**, Robert V. Dennis, Vincent Lee, and Sarbajit Banerjee*
University at Buffalo, SUNY, Buffalo NY
Graphene Nanocomposites as Anti-Corrosive Materials
- Poster 19.** **Yi Xin Ren**, Kristin Butterworth, Robert L. DeLeon and James F. Garvey*
University at Buffalo, SUNY, Buffalo, NY
Chemical reactivity, bonding and structure of the nucleophilic substitution of p-chlorofluorobenzene ions by ammonia

- Poster 20.** **Nathan T. Scharf** and Markus M. Hoffmann*
The College at Brockport, SUNY, Brockport, NY
Ion-pairing of the ionic liquid 1-hexyl-3-methylimidazolium bis(triflyl)amide in chloroform
- Poster 21.** **Miso Gostimir**, David Adams, Mary-Ann Endoma-Arias, Sergio Alatorre, Tyler Bissett, Setu Gupta, Jordan Froese, Hollich Ho, Jon Scattolon, Vimal Varghese, Sergey Vshyvenko, Ian Taschner, John Trant and Tomas Hudlicky*
Brock University, St. Catharines, ON
Recent Advances in Chemoenzymatic Synthesis
- Poster 22.** **Erica Salem**, Nathan Guterry, Ivonne M. Ferrer and Luis A. Colon*
University at Buffalo, SUNY, Buffalo, NY
Zirconia and Hafnia Monolithic Structures for Electrokinetic Micropumps
- Poster 23.** **Robert W. Kubiak II** and Dominic L. Ventura*
D'Youville College, Buffalo, NY
Metallophthalocyanines as a Catalyst in Cyclopropanation Reactions
- Poster 24.** **John Spaulding**, B. Schultz and Sarbajit Banerjee*
University at Buffalo, SUNY, Buffalo, NY
Investigation of Synthesis and Transfer of Single-Layered Graphene by Raman Spectroscopy
- Poster 25.** **Adam A. Szymaniak**, **Ryan C. Cotroneo** and Fehmi Damkaci*
SUNY Oswego, Oswego, NY
Total Synthesis of Hyperglycemic Drug Rosiglitazone (Avandia): Protocol for Advanced Chemistry Laboratory
- Poster 26.** **Laurine Zupp**, **Veronica Campanella** and Ronny Priefer*
Niagara University, Niagara University, NY
Microwave Irradiation and Silica-gel Bound reagents in Friedel-Craft Alkylation
- Poster 27.** **Marat Mitelman**, Benjamin W. Turnpenny, and Sherry R. Chemler*
University at Buffalo, SUNY, Buffalo, NY
Synthesis of Isoxazolidines via Copper (II) Promoted Intermolecular Diamination of Hydroxylamine Olefins
- Poster 28.** **Derek Zemla**, Adam Dannenhoffer, Nicholas Pantano, Steven Szczepankiewicz and Mariusz Kozik*
Canisius College, Buffalo, NY
Direct NMR Evidence for Dimer Formation by Transition Metal Substituted Polyoxometalates in Nonpolar Solvents

Poster Abstracts

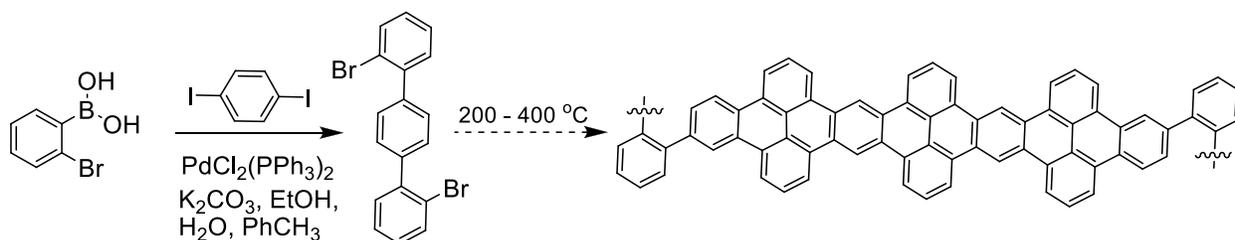
Poster 1.

Dibromo Precursor Synthesis for the Bottom-Up Fabrication of Graphene Nanoribbons

*Deena Butryn and David G. Hilmey**

Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY

Graphene nanoribbons (GNRs) are unrolled single-walled carbon nanotubes. Bottom-up fabrication of GNRs allow for atomically precise structures controlled by the synthesis of precursor monomers. The synthesis of different halogenated precursor monomers will allow for unique GNR topologies and widths. A method to produce these molecules with unique backbones has been developed. The syntheses of 1,5-dibromonaphthalene and 1,4-bis(2-bromophenyl)benzene, through aromatic bromination and Suzuki coupling, will be subjected to diradical coupling and dehydrocyclization to produce the desired GNRs. Additional monomer unit syntheses are currently underway. GNRs have desirable electronic structures and would be useful in nanoelectronics as they possess semi-conductive properties and may be technological alternatives to silicon semiconductors.



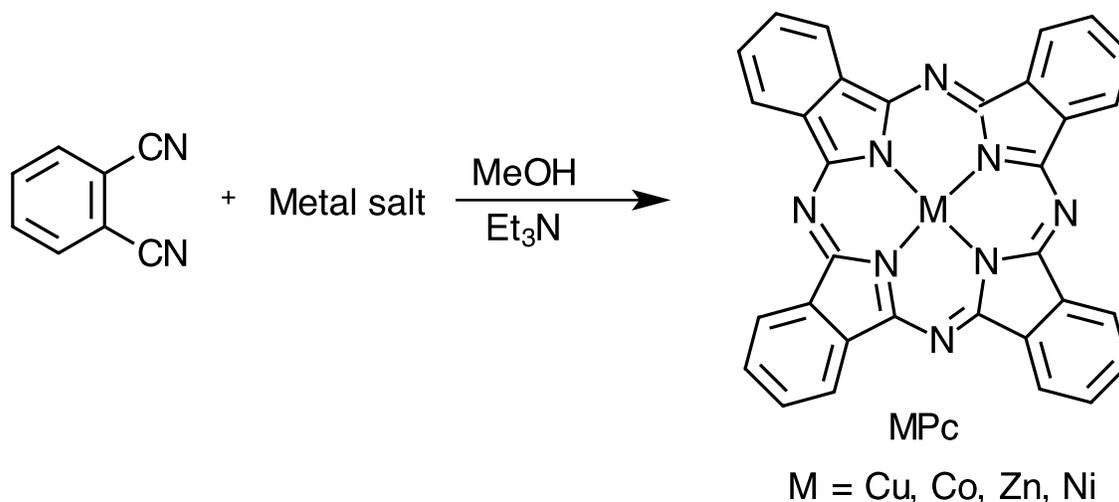
Poster 2.

Novel Mild Synthesis of Metallophthalocyanines

*Carly Mazuca and Dominic L. Ventura**

Math and Natural Sciences Department, D'Youville College, Buffalo, NY

Phthalocyanines have been synthesized via several procedures, though most utilize vigorous reaction conditions. It was our goal to construct a milder synthetic route with good yields to synthesize the desired metallophthalocyanines. Utilizing inexpensive mild reagents and varying reaction conditions, a new synthesis of the metallophthalocyanine has been achieved.



Poster 3.

Synthesis of Stimuli-Responsive Linkers for use in Silica Multifunctional Drug-Delivery Agents

*Zackary Falls, Jamie Hitro and Jeremy Steinbacher**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

Novel drug-delivery agents are needed to overcome the limitations of systemic toxicity of traditional chemotherapeutics. An even more powerful paradigm combines delivery and imaging into one agent, so called theranostic materials (for “therapeutic” and “diagnostic”). One potential platform for such an agent is nano- or microparticles consisting of porous silica, a well-characterized material with minimal toxicity and with great flexibility for chemical functionalization. Many theranostic systems, including those based on silica, depend on triggers from biologically-relevant stimuli to effect the release of a payload or the activation of some imaging modality. Such stimuli include a decrease in pH in tumor stroma or the reducing conditions in intracellular environments. To date, most reports have relied on an *ad hoc* approach to stimuli-responsive triggers, with new chemistries developed for each application. We hope to advance the field by developing a set of universal, stimuli-responsive linkers for use with silica theranostic agents. We have designed and are currently synthesizing organoalkoxysilanes that are cleaved under acidic conditions or under reducing conditions. These silanes contain either an azide or a terminal alkyne, making them reactive in the high-yielding “click” reaction of the Huisgen dipolar cycloaddition. Because many potential payloads (MRI contrast agents, chemotherapeutics, etc) are available with complementary click handles, our silanes will allow for the functionalization of any silica theranostic agent with pH- or redox-cleavable payloads.

Poster 4.

Copper-Catalyzed Intramolecular Alkene Carboetherification/Intermolecular Heck-Type Coupling Cascade

*Nicole E. Kendel and Sherry R. Chemler**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Carboetherification is the simultaneous formation of carbon-oxygen and carbon-carbon bonds across an olefin. This methodology is an attractive method for the synthesis of substituted oxygen heterocycles. Utilizing previously determined optimized reaction conditions, a range of simple alcohol substrates were examined. Current study involves expansion of the range of vinyl arenes to include styrene, α -methyl styrene and benzofuran. This methodology has potential use in the synthesis of biologically active compounds and natural products.

Poster 5.

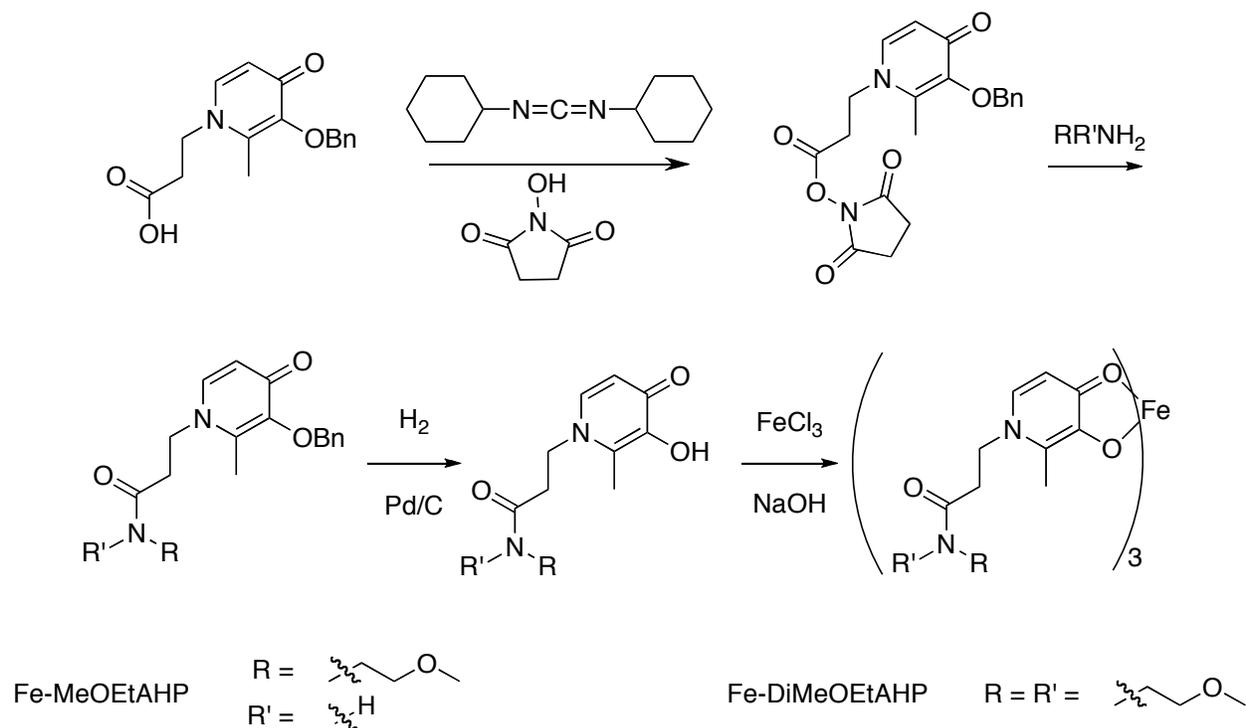
Improved Syntheses of Amide Hydroxypyridinone Ligands for use as Contrast Agents for Magnetic Resonance Imaging (MRI)

Tracey Lewandowski¹, Nicholas P. Richardson² and Daniel D. Schwert^{1*}

¹St. John Fisher College, Rochester, NY

²Wagner College, Staten Island, NY

MRI is used for imaging soft tissue. A contrast agent can be used during MRI to help to produce a brighter, sharper image to help to distinguish between healthy and diseased tissues. This work will help to increase the knowledge and research on iron(III) based contrast agents. Two ligands were synthesized (MeOEtAHP and DiMeOEtAHP) for use as chelates for iron(III). Synthetic intermediates were isolated and purified. A coupling reaction with DCC and *N*-hydroxysuccinimide was used to synthesize the ligands from 1-(2'-carboxyethyl)-2-methyl-3(benzyloxy)-4(1H)-pyridinone and the corresponding amines. The ligands were characterized by NMR spectroscopy. The physical properties of the ligands and their iron(III) complexes were studied to determine their relaxivity (r_1) values in water and an HSA solution. It was found that the relaxivity value of Fe-MeOEtAHP increased slightly in HSA; whereas the relaxivity value of Fe-DiMeOEtAHP decreased in HSA.



Poster 6.

Synthesis of N-carboxamidine spermine and spermidine derivatives and inhibiting effects on *Trypanosoma cruzi* trypanothione reductase

*Jessica L. Stachowski, Andrew C. Forrestel, Jesse G. Fodero and Mary C. O'Sullivan**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

Protozoan parasites that are members of the family Trypanosomatidae cause human diseases including Chagas' disease in South America (*Trypanosoma cruzi*) and trypanosomiasis in Africa (*T. brucei* subspecies). Trypanosomatids have a unique antioxidant metabolism in which the enzyme, trypanothione reductase (TR), plays a central role. This enzyme catalyzes the NADPH reduction of the disulfide of trypanothione. Trypanothione is an unusual glutathione-spermidine conjugate (N^1, N^8 -bis(glutathionyl)spermidine) and the reduced (dithiol) form of trypanothione acts as a reducing agent in several vital processes including maintenance of the parasites' cellular thiol redox balance and reduction of tryparedoxin (which is a substrate for ribonucleotide reductase). Thus inhibitors of TR have potential as novel anti-trypanosomal chemotherapeutics. Here we report the syntheses of several novel polyamines, and studies of the inhibiting effects of these compounds on recombinant *T. cruzi* TR. The polyamines investigated were spermidine (N -(3-aminopropyl)-1,4-diaminobutane) and spermine (N, N' -bis(3-aminopropyl)-1,4-diaminobutane) derivatives with N -carboxamidine and aromatic substituents.

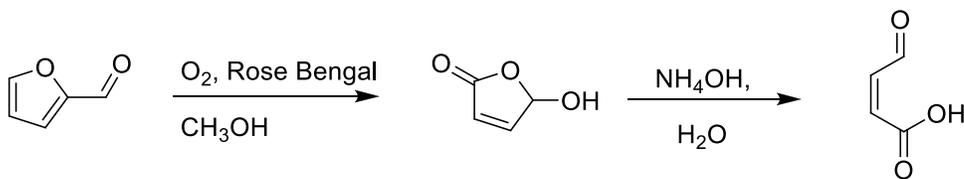
Poster 7.

Synthesis of Maleamic Acid Amidinohydrolase Small Molecule Analogs

*Kelly R. Morrison, Deena Butryn and David G. Hilmey**

Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY

The oxidative degradation of niacin (vitamin B₃) to fumarate in several species of aerobic bacteria includes the hydrolytic deamination of maleamate to maleate, catalyzed by maleamate amidohydrolase (NicF). NicF has been recently crystallized from *Bordetella bronchiseptica* by Dr. Mark Snider and Dr. Roger Rowlett. A hydrolysis mechanism associated with NicF is proposed, but currently unknown. The development of small molecule inhibitors which are structurally similar to maleamate should help define the active site organization and mechanism of action of NicF. Analog synthesis has focused on structures mimicking hydrogen bonding potential and carbonyl polarity for binding without introducing potential enzyme reactivity. Synthesis began from furfural to produce the lactone 5-hydroxyfuran-2(5H)-one, the first substrate analog. Hydrolysis of the lactone with ammonium hydroxide in water produced 3-formyl acrylate as a second potential analog. Reduction of the aldehyde should produce the corresponding alcohol and third potential analog. Additional syntheses to the above compounds and a fourth compound, which replaces the amido group with a boronate moiety, are also in progress.



Poster 8.

Copper(II) Catalyzed C-H Amination: Synthesis of Enamines

*Garrick H. Zibreg, Tim W. Liwosz, Sherry R. Chemler**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

The purpose of this research is the synthesis of enamines by catalyzing the bond formation of sulfonyl protected nitrogens across an olefin. Unlike other metal catalysts that perform similar reactions, copper is inexpensive and could lower the synthesis cost of enamines. The reactions are catalyzed by a copper(II) triflate complex utilizing achiral bisoxazoline as the ligand with stoichiometric amounts of inexpensive MnO₂ over 24 hours. Optimization of the reaction has further reduced the cost by indicating that 20 mol% copper is more efficient than 30 mol% and that base is not necessary, unlike similar reactions. Applications of this reaction could be found in reducing the cost of synthesizing biologically active enamine containing organic compounds.

Poster 9.

What Makes Lyme Disease Tick? Preparation and Characterization of the Global Regulator, BosR

*Elisabeth A. Geyer and Sarah E. Evans**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

Caused by the bacteria *Borrelia burgdorferi*, Lyme disease is the fastest growing and most common tick-borne illness in the United States. Vital to the survival of *B. burgdorferi* in ticks and vertebrates, *Borrelia* oxidative stress regulator, BosR, is a regulatory transcription factor that functions to activate and repress nearly 80 genes, including genes for DNA protection from damage during starvation or oxidative stress and control over the expression of outer membrane proteins. Believed to be a member of a family of metalloregulatory proteins known as Fur, ferric uptake regulator, little has been discovered about the important role and types of metal ions that are thought to function in the regulatory pathway of BosR. Future work will include a broad characterization of BosR by metal binding titrations with UV-Visible spectroscopy, circular dichroism spectroscopy, tryptophan fluorescence studies and inductively coupled plasma-mass spectrometry. Electromobility shift assays and fluorescence anisotropy assays will be performed to investigate DNA binding properties and possible classification of a Bos box. In this work, focus is placed on the preparation, purification and initial characterization of the protein of interest.

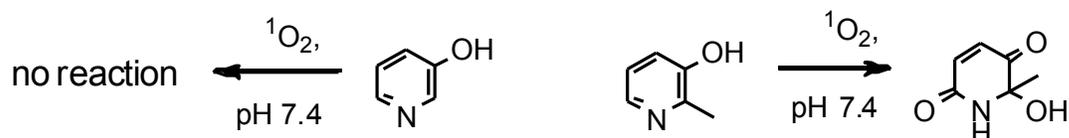
Poster 10.

An Investigation of the Structural Requirements for the Antioxidant Activity of Vitamin B₆ through Pyridoxine Analogs

*Aashish Abraham, David Samuel and David G. Hilmey**

Department of Chemistry, St. Bonaventure University, St. Bonaventure, NY

Previous research has shown that Vitamin B₆ has antioxidant activity, however the mechanism through which the compound reacts with singlet oxygen is not completely understood. We have proposed and begun synthesis of Vitamin B₆ analogs to see how the loss of certain functional groups around the pyridine ring affects its antioxidant activity; specifically, the loss of either the 4'-hydroxymethyl, 5'-hydroxymethyl, or 2'-methyl groups, or a combination of these. The singlet oxygen reactions are run in either a D₂O buffer or methanol-d₄ solvent. In the initial example, 3-hydroxy-2-methylpyridine was exposed to green light and Rose Bengal dye under an oxygen atmosphere to generate singlet oxygen. NMR analysis shows that there are multiple products being formed and appears to involve oxidation of the 2- and 6-positions of the original pyridine ring. To increase selectivity, the reaction was run at 0 °C resulting in a primary product capable of characterization by 1D and 2D NMR spectroscopy. We hypothesize that the 2'-methyl substituent coming off the ring is crucial to the progression of the reaction. Syntheses of further pyridoxine analogs have commenced and are also described.



Poster 11.

Synthesis and multilayering of novel pseudo-polyelectrolytes into thin films

*Marie E. Albano, Chelsea L. Recor, Megan McGahan and Ronny Priefer**

Department of Biochemistry, Chemistry, and Physics, Niagara University, NY

Multilayered systems containing strong polyelectrolytes (SPE) have been acknowledged by the scientific community. Even multilayered systems with weak polyelectrolytes have been published. However, multilayering with a pseudo-polyelectrolyte (pPE) is a fairly recent branch of these systems. In systems created with pPE's, the chemical interactions within the system more so than those already established. To date, there are only two known pPE that have been multilayered. We have been able to introduce another pPE's, into this promising field, poly(4-vinylbenzene boronic acid) (PVBBA). A fourth pseudo-polyelectrolyte, poly(4-vinylperbenzoic acid) (PVPBA), is being examined for its potential in multilayered systems. As with previously reported, the unique properties of pPE's allow only a very narrow range of assembly pHs to be accessible when multilayered with both the WPE, poly(allylamine hydrochloride) (PAH), and the SPE, poly(diallyldimethylammonium chloride) (PDADMAC). In addition, we have been investigating the WPE, poly(4-vinylbenzoic acid) (PVBA). Multilayered systems for PVBA were produced at pHs 6, 7, 8, 9, 10, and 11 and a linear growth in absorbance readings with increasing layer number was observed. This latter system will help us understand multilayered films created with PVPBA; in which the systems have the potential of producing a strongly antimicrobial surface.

Poster 12.

Cyclopropanation-cross-coupling strategy for synthesis of chiral alkylidene cyclopropanes

*Russell F. Algera, David J. Fortman and Timothy M. Gregg**

Department of Chemistry and Biochemistry, Canisius College, Buffalo, NY

Our methodology for the enantioselective cyclopropanation of allenes takes advantage of silicon-, tin- and boron-substituted allene substrates, resulting in enantiomerically enriched silyl-, stannyl- and borono-alkylidene cyclopropanes. We have previously observed that both tin and silicon moieties serve to enhance the rhodium-catalyzed cyclopropanation of allenes by increasing the reaction rate over that of allenes with only carbon substituents. We now show that the resulting stannyl methylidene cyclopropanes are good substrates for Stille coupling, opening the possibility of constructing a wide variety of vinyl- and aryl-substituted methylidene cyclopropanes from a single common substrate. A similar coupling strategy is under development mediated by Hiyama-type silicon to palladium vinylidene group transfer. Until now, boronoallenes have not been observed to undergo 2+1 cyclopropanation, and we demonstrate that a one-pot cyclopropanation/Suzuki cross-coupling sequence has promise for constructing densely functionalized chiral intermediates.

Poster 13.

Chromatographic Separation of Graphene Oxide Nanomaterial

Allen K Bourdon, Luis A. Colon, Cody Vinci, Ivonne M Ferrer, Lisandra Santiago, Amber Moore, Chi Man Ng, Sowjanya Garapati, Zuchin Xue, Jazmine Holmes, Erika Salem, Brian Tobahzinski and Nathan Guterry*

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Since the discovery of isolated graphene obtained from simple mechanical cleaving ‘Scotch tape method,’¹ the study of graphene based materials has expanded in multiple directions. A current synthetic technique for obtaining graphene begins with a graphite starting material that must be oxidized for an extended period at high temperature, under reflux, using a strong acid. Following oxidation, the graphene oxide is exfoliated and filtered in order to retrieve the desired nano-sized material. These carbon-based nanomaterials have been isolated by chromatographic separation using high-pressure liquid chromatography. The importance of this study is based on the photo luminescent properties of the separated fractions of nanomaterials. These quantum fluorescent properties could serve useful in applications such as nanotechnology, biosensing, and drug delivery.^[2-4]

1. Novoselov, K. S. et al. Electric field effect in atomically thin carbon films. *Science* 306, 666 – 669 (2004).
2. T. D. Burchell, *Carbon materials for advanced technologies*, Pergamon, New York, 1999.
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Poster 14.

Fourier Transform Microwave Spectroscopy of Alkali Metal Hydrosulfides: Detection of KSH

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Fourier transform microwave (FTMW) spectroscopic techniques have been used to record pure rotational spectra of potassium hydrosulfide in its ground electronic state. This study represents the first gas phase spectroscopic observation of KSH. FTMW spectra of NaSH were also recorded. The metal hydrosulfides were produced by discharge assisted laser ablation of the solid alkali metal in the presence of hydrogen sulfide or deuterated hydrogen sulfide. Rotational transitions in the 5 – 20 GHz range were measured and hyperfine splittings due to the alkali metals and deuterium were resolved. Rotational as well as metal and deuterium quadrupole coupling constants have been determined from the data. The hyperfine parameters will be interpreted in terms of metal-ligand bonding character. Geometric parameters of the alkali metal hydrosulfides will be compared.

Poster 15.

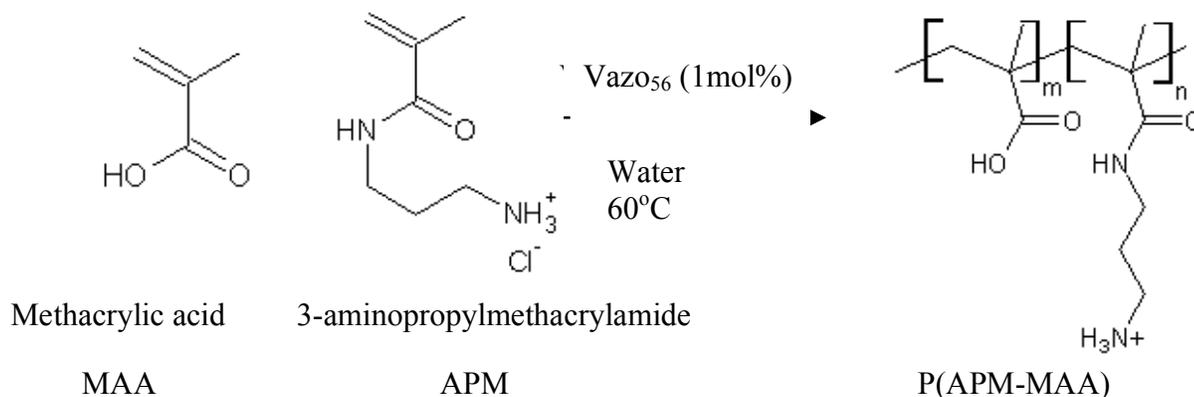
Synthesis and characterization of polyampholytes for use in cell-encapsulation

*Ankita Dubey, Nicholas A. D. Burke and Harald D. H. Stöver**

Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON

Immunoisolation of hormone or enzyme producing cells by microencapsulation is an approach for treating conditions such as diabetes, neurological disorders (Parkinson's, Alzheimer's) and various other hormone and enzyme deficiency disorders.

There is considerable interest in the development of synthetic polymers for use as biomaterials and our group has focused on polymers for use in cell encapsulation, in particular, those able to form covalently cross-linked networks. These materials must be biocompatible with the encapsulated cells and with the host following implantation. One desirable feature is that they be resistant to protein binding as this can often be a first step in an immune response. Zwitterionic polymers, those bearing both positive and negative charges, have shown promise as protein resistant materials and they are known to have solubility properties that are very sensitive to solution pH and ionic strength as well as the polymer composition. In this paper, the preparation and properties of polyampholytes (a type of zwitterionic polymer) based on 3-aminopropylmethacrylamide (APM) and methacrylic acid (MAA) will be described. This work required finding conditions that allowed the preparation of different copolymer compositions without significant compositional drift during polymerization. The remarkably sensitive solubility properties of these copolymers to factors like pH, ionic strength and temperature will be discussed. In addition, the results of preliminary attempts to form covalently cross-linked networks by the combination of polyampholytes with reactive copolymers bearing electrophilic groups capable of reacting with the amino groups of the polyampholyte will be presented.



Scheme 1: Showing Free radical copolymerization of APM and MAA in water

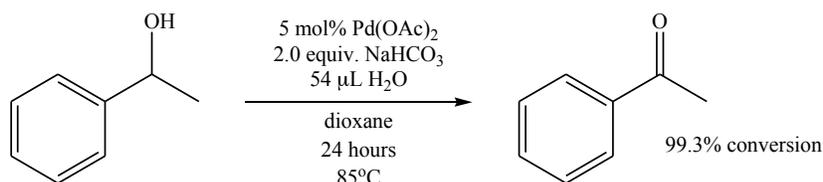
Poster 16.

Palladium Catalyzed Reactions: A Search For A Greener Oxidation Pathway

*Shannon Hritz, Adam Townley, Nathalie VanderRijst, Hillary Chartrand, Melissa Rosenburg, Scott Macbeth, Yoon-Kook Kim, and Karen E. Torraca**

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One of the standard reactions used to generate aldehydes and ketones is the direct oxidation of alcohols. Many current synthetic methods for completing these reactions have significant disadvantages for large-scale manufacture such as the use of stoichiometric amounts of heavy metals, hazardous reagents, and solvent-intense extractive work-ups. In light of this, our research is focused on developing a mild and green oxidation method that could be implemented at large scale. Our efforts focused on the oxidation of 1-phenylethanol to acetophenone. This research sought to minimize the formation of the side product ethyl benzene and attain high conversions consistently using palladium catalysis. Various amounts and types of reagents were tested for their effect. The most successful reaction conditions were:



High conversions were only achieved by blanketing the reaction with argon for an hour and then removing the argon hose to allow the reaction mixtures to vent. This reaction method was also applied to other alcohols. Future research will focus on understanding the mechanism of this reaction, varying the amount of water used, and further experimentation with different alcohols.

Poster 17.

Self-assembly of Amyloid Beta Peptide Over Dialkoxo Disulfide Functionalized Nano Gold Colloidal Particles

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¹Department of Chemistry, SUNY Geneseo, Geneseo NY

²Department of Chemistry, Biochemistry, and Physics, Niagara University, NY

Aiming to more stably produce an oligomer form of amyloid beta (i.e., a key intermediate of fibrillogenesis which eventually leads to Alzheimer's disease), the surface of gold colloids were functionalized with nitro-, phenyl-, chloro-, and methoxy-dibenzyloxy disulfide, and molecular interactions were investigated in a dimethyl sulfoxide environment. The transition of color change was observed at pH_0 as the pH value was lowered externally. As evidence of disulfide being adsorbed on the colloidal surface, the pH_0 values were dependent of each substituent of the dibenzyloxy disulfide compounds. The trend of pH_0 exhibited a parabolic relationship as a function of F-value (Swain-Lupton Field constant). Functionalization of gold colloidal surface with methoxy-dibenzyloxy disulfide achieved larger amplitude in repetitive peak shift between pH 4 and 10 implying a formation of an oligomer under the reversible process.

Poster 18.

Graphene Nanocomposites as Anti-Corrosive Materials

*Steven M. Henderson, Robert V. Dennis, Vincent Lee, and Sarbajit Banerjee**

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Graphene is a single layer of sp^2 -hybridized carbon atoms arrayed in a honeycomb lattice, and has been the subject of very intense research in recent years due to its remarkable properties. Due in large part to the extensive delocalization of its π -bonds, graphene has exceptional mechanical, thermal, and electronic properties, including high tensile strength, tunable surface energetics, and high electrical conductivity. The properties of graphene have led to increased interest in many practical applications and among these are as fillers in nanocomposites. Herein we present a graphene/polyetherimide nanocomposite system, which has been designed for use as an anti-corrosive coating for protection of low alloy steel. These coatings have been designed to manifest an active-passive approach to preventing corrosion of the underlying metal surface. Indeed, even at relatively low concentrations, the addition of graphene to the nanocomposite induces an appreciable improvement of the coating's resistance to corrosion; seen as a reduction in the corrosion rate of steel samples under accelerated testing conditions.

Poster 19.

Chemical reactivity, bonding and structure of the nucleophilic substitution of p-chlorofluorobenzene ions by ammonia

*Yi Xin Ren, Kristin Butterworth, Robert L. DeLeon and James F. Garvey**

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The chemical reactivity within gas phase p-chlorofluorobenzene-ammonia heterocluster cations $\{(ClFC_6H_4)_m-(NH_3)_{n=1-8}\}^+$ have been investigated via a triple quadrupole mass spectrometer and through DFT calculations. Collision induced dissociation (CID) experiments were performed in which mass selected cluster ions are accelerated into a cell containing argon gas and the resulting products then subsequently mass analyzed. Two interesting reaction results are observed. The first is that the 1:1 peak is missing. Further investigation is underway to find out why this is the case. The second is survey from the CID experiments display the magic number for $(ClFC_6H_4)_6^+$ with helium gas. The reactions between p-chlorofluorobenzene cation and ammonia involve intra-cluster proton transfer of ammonia giving clusters of high stability.

Poster 20.

Ion-pairing of the ionic liquid 1-hexyl-3-methylimidazolium bis(triflyl)amide in chloroform

*Nathan T. Scharf and Markus M. Hoffmann**

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In prior research, long-lived ion-pairing of the Ionic Liquid (IL) 1-ethyl-3-methylimidazolium bis(triflyl)amide (**1**) has been observed in chloroform at dilute concentrations as evidenced by two sets of resonances in the ^1H NMR spectrum (*J. Sol. Chem.* **2004**, 33, 381-394). A closely related IL, 1-hexyl-3-methylimidazolium bis(triflyl)amide (**2**) that contains a larger side chain (hexyl versus ethyl) does not show two separate resonance sets in ^1H NMR. Does (**2**) still form ion pairs at dilute concentrations in chloroform? In order to answer this question, we explored the concentration dependence of the self-diffusion coefficients of the cation and anion measured by ^1H and ^{19}F Diffusion ordered spectroscopy (DOSY). If there is no ion-pairing then the cation and anion should have separate self-diffusion coefficients. In addition, at low concentrations where the viscosity has only small effects on the self-diffusion, we would expect the self-diffusion coefficient to be concentration independent. However, we observed continually increasing diffusion coefficients even for concentrations as low as 0.001 M, and the diffusion coefficients for the cation and anion remained identical regardless of solution concentration. Furthermore, independent viscosity measurements allowed us to estimate the radii of the diffusing species using the Stokes-Einstein equation. The radii increased with increasing concentration indicating a shift in equilibrium towards the ion-paired species. The values of the radii were too small to allow for the presence of higher aggregates. Interestingly, we observed a maximum for the apparent radius at about 0.1 M. Given that increasing IL concentration should favor formation of ion-pairs and possibly higher aggregates, this observation of a maximum indicates a change in the solution structure for concentrations above 0.1 M, which will be discussed.

Poster 21.

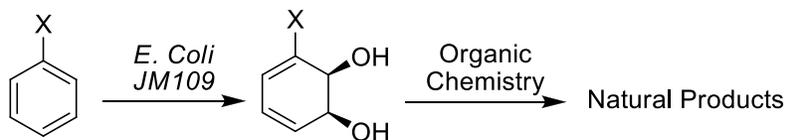
Recent Advances in Chemoenzymatic Synthesis

*Miso Gostimir, David Adams, Mary-Ann Endoma-Arias, Sergio Alatorre, Tyler Bissett, Setu Gupta, Jordan Froese, Hollich Ho, Jon Scattolon, Vimal Varghese, Sergey Vshyvenko, Ian Taschner, John Trant and Tomas Hudlicky**

Department of Chemistry, Brock University, St. Catharines, ON

The microbial oxidation of aromatics by *P. Putida* F1 or *E. Coli* JM109 (pDTG601) is a reaction which has no equivalent in the realm of traditional reagent chemistry. The enzymatic oxidation provides homochiral starting materials in which each carbon atom may be further functionalized. The utility of *cis*-cyclohexadiene diol derived from microbial oxidation of aromatic hydrocarbons in asymmetric synthesis is firmly established.¹ Since the first application of *cis*-cyclohexadiene diols in the synthesis of pinitol by Ley in 1987², over 400 metabolites have been isolated. Many of these have found application in the synthesis of oxygenated natural products or analogues.

Other work currently underway in the Hudlicky group involves the exploration of new methodologies, both chemical and enzymatic, applicable to the total synthesis of complex natural products. These methodologies include vinylcyclopropyl [5+2] cycloaddition reactions, the application of *R. eutrophus* B9 to the synthesis of natural products and a symmetry-based approach to the morphinan skeleton.



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2. Ley, S. V.; Sternfeld, F.; Taylor, S. *Tetrahedron Lett.* **1987**, *28*, 225.

Poster 22.

Zirconia and Hafnia Monolithic Structures for Electrokinetic Micropumps

*Erica Salem, Nathan Guterry, Ivonne M. Ferrer and Luis A. Colon**

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There is a constant need for the development of new technology that can provide ways to reduce weight and space requirements when pumping fluids. With the challenge of reutilizing all available fluids in a mission, there is great interest in recovering water and ammonia from human urine, as well as the use of effective fuel cells. The use of electrokinetic (EK) pumps would favor over conventional pumping systems because of its simplicity, lightweight, and compact size. EK pumps are a new technology that allow for liquid to be propelled by means of electro-osmosis, eliminating the need for pressure to transport fluids and allowing for a more effectively use of space. The majority of the current EK pumps are based on fluid transport through porous silica materials, which have shown to have limitations. We are exploring the use of hafnia and zirconia monoliths as the pumping elements for various solutions, including 100% methanol, 98% methanol, 50% methanol, 25% methanol, water, and ammonium hydroxide to determine flow rate ($\mu\text{L/s}$) as a function of voltage, from 5V to 25V. The tests are conducted with an apparatus run by batteries. Increasing the applied voltage linearly increases the flow rate with both monolithic structures. Our findings indicate that the typical flow rates achieved with the hafnia monolith are comparable to those of the silica monoliths. The flow rates achieved on zirconia monoliths, however, are significantly higher than those obtained on silica or hafnia monoliths. Details of our investigations will be the focus of this presentation.

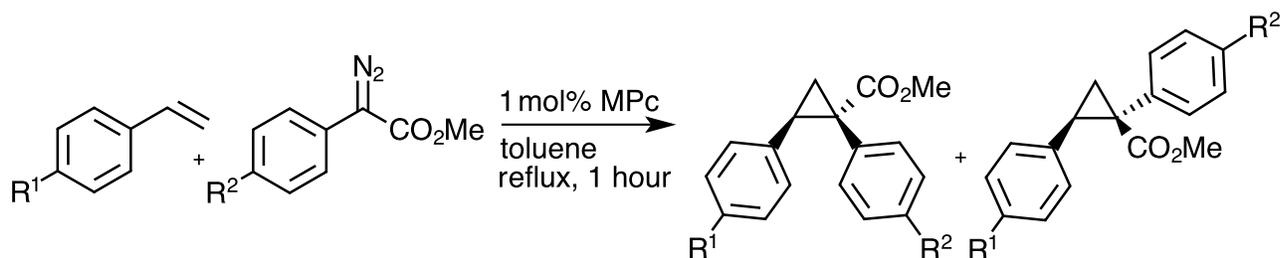
Poster 23.

Metallophthalocyanines as a Catalyst in Cyclopropanation Reactions

*Robert W. Kubiak II and Dominic L. Ventura**

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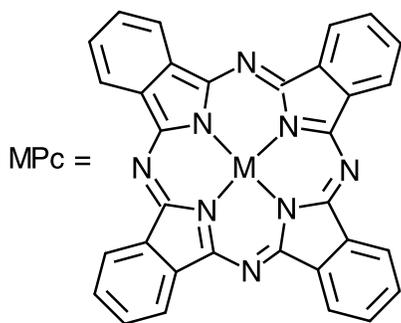
Metallophthalocyanine catalyzed cyclopropanation reactions have had little attention to date. The yields and diastereoselectivity of these reactions are influenced by the nature of the styrene as well as the aryldiazoacetate and catalyst. The products have been synthesized in good yields (up to 74%) with high diastereoselectivity (up to 17:1 ratio cis: trans products).



up to 17:1 ratio cis:trans

R¹ = H, Me, OMe, Cl, CF₃

R² = H, Me, OMe, Br, Cl



M = Cu, Co, Zn, Ni

Poster 24.

Investigation of Synthesis and Transfer of Single-Layered Graphene by Raman Spectroscopy

*John Spaulding, B. Schultz and Sarbajit Banerjee**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Graphene, a network of sp^2 -bonded carbon atoms arranged in a honeycomb-like lattice, is currently the thinnest and strongest material known to man. The two-dimensional geometry of graphene results in a large delocalized cloud of electrons that make graphene highly conductive, and provides the potential for ballistic conduction. Graphene's unusual properties hold tantalizing potential for applications in high-frequency electronics, interconnects, transistors, and touch-screen devices, to name a few. Much progress has been achieved with the synthesis of large-area high-quality graphene but arguably the most facile and inexpensive approach involves the catalytic decomposition of hydrocarbon precursors on metal foils at high temperatures. Unfortunately, most of the transfer processes that have been developed are prone to damaging the structure of graphene. The introduction of folds, ripples, or holes to the graphene sheet impedes the flow of electrons by giving rise to Coulomb scattering sites, thus decreasing conductivity. In order for any meaningful investigations of electronic transport behavior in graphene to be performed, high-fidelity methods of transfer must be developed that preserve the graphene structure and thus the unique electronic properties of single-layered graphene. We present here an approach to grow graphene on transition metal substrates, primarily nickel and copper, in a hot-walled tube furnace via the thermal decomposition of hydrocarbons at high temperatures. We have further devised transfer techniques that are based on the idea that conformal adhesion of a pliable substrate to the top surface of graphene prior to etching of the underlying metal substrate can lead to graphene sheets with fewer defects after transfer. Raman spectroscopy and optical micrographs of graphene transferred to 300 nm SiO_2/Si are presented with a focus on the quality of graphene before and after transfer.

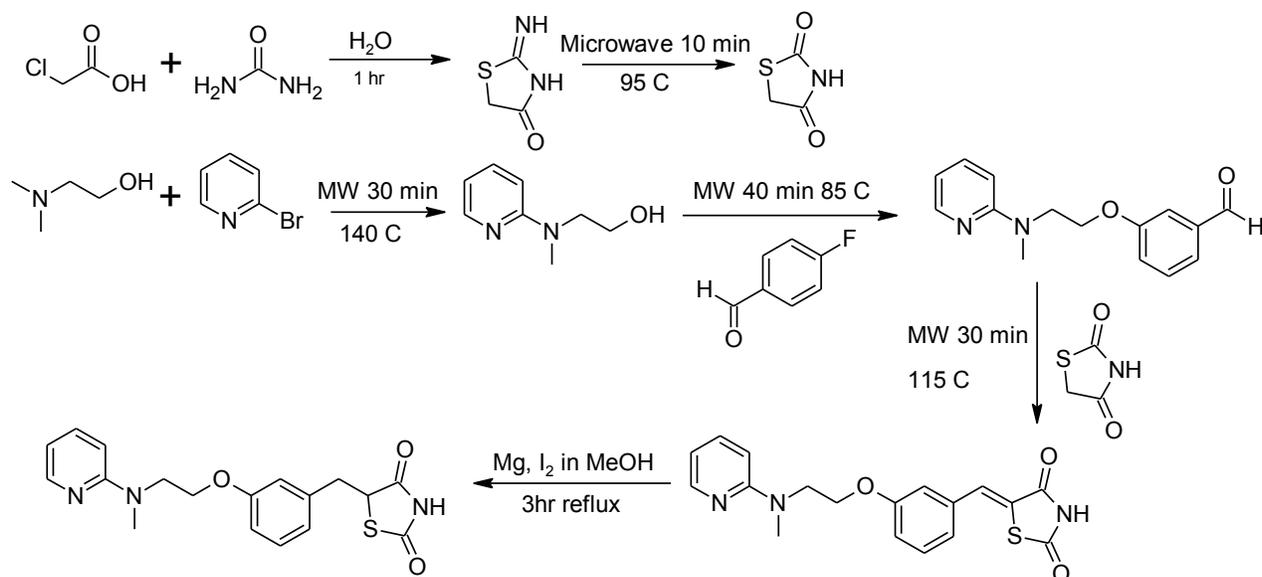
Poster 25.

Total Synthesis of Hyperglycemic Drug Rosiglitazone (Avandia): Protocol for Advanced Chemistry Laboratory

*Adam A. Szymaniak, Ryan C. Cotroneo and Fehmi Damkaci**

Department of Chemistry, State University of New York at Oswego, Oswego, NY

The utilization of microwave chemistry with shorter reaction times and increased yield has assimilated efficiently into the discipline of medicinal chemistry, more specifically pharmaceutical development. The total synthesis of the hyperglycemic drug Rosiglitazone (Avandia) was achieved in six steps, and four were performed under microwave irradiation. The synthesis has been adopted from a literature procedure to be used for advanced chemistry laboratory curriculum. The goal for the protocol was to perform each step in sufficient time for a lab period, combined with the necessity for excess intermediates for subsequent steps in lieu of mistakes. This was accomplished through manipulating molar equivalents, batch irradiating vials and modifying work-up procedures amongst other things. Rosiglitazone was synthesized using “green chemistry,” relating to the use of microwave irradiation, obtaining an overall yield of 40% crude product.



Poster 26.

Microwave Irradiation and Silica-gel Bound reagents in Friedel-Craft Alkylation

*Laurine Zupp, Veronica Campanella and Ronny Priefer**

Department of Biochemistry, Chemistry, and Physics, Niagara University, NY

The use of microwave chemistry to accelerate reactions has been an increasingly popular technique used in organic chemistry synthesis since the 1980's. There are many publications on the "specific microwave effect" but there is new research supporting the increased reaction rates being a purely thermal event. This theory states the shorter reaction times are achieved because the radiation given off from the microwave is converted to heat, allowing it to produce a "superheating" site. This drastically increases the rate of reactions.

Another relative recent technique used in organic chemistry is the use of solid support reagents. Silica gel bound reagents are known to exhibit unique improvements over traditional means of performing chemical reactions. The benefit of this approach is that upon completion of a reaction, a simple filtration can be performed which expedites the work-up and produces less organic waste. Since these simple work ups are solvent free, it is thought that they can easily be scaled up for pharmaceutical use.

Friedel-Craft alkylation has been explored using microwave chemistry as well as with solid-support bound reagents, however never in combination. Our research then focuses on combining these techniques for faster simpler reactions, which have higher yields than their conventional methods. We have begun to evaluate the use of varying alkylation reagents with both AlCl_3 and Si-AlCl_x as the catalysts under microwave irradiation. These reactions conventionally take 24 hours, but they went to completion in only 5 minutes when placed in the microwave.

Poster 27.

Synthesis of Isoxazolidines via Copper (II) Promoted Intermolecular Diamination of Hydroxylamine Olefins

*Marat Mitelman, Benjamin W. Turnpenny, and Sherry R. Chemler**

Department of Chemistry, University at Buffalo, SUNY, Buffalo, NY

Using hydroxylamine olefins as substrates for copper (II) promoted intermolecular diaminations; it is possible to synthesize isoxazolidines, a synthetically important moiety in the pharmaceutical industry. Current reaction conditions give yields of 71% with only two equiv. of copper (II) ethylhexanoate. Reaction conditions are currently being optimized for different substrates to allow for using catalytic amounts of copper in the diaminations. The Chemler Group has reported several different intermolecular copper (II) catalyzed diamination reactions.

Poster 28.

Direct NMR Evidence for Dimer Formation by Transition Metal Substituted Polyoxometalates in Nonpolar Solvents

*Derek Zemla, Adam Dannenhoffer, Nicholas Pantano,
Steven Szczepankiewicz and Mariusz Kozik**

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Our recent work demonstrated that structures of Transition Metal Substituted Heteropoly Tungstates (TMSHT) in nonpolar solvents are more complex than published in the literature. Phase transfer of TMSHT's, which is accomplished by mixing the potassium salt of TMSHT in water with tetraheptylammonium bromide in toluene, also causes some KBr to be transferred into the toluene phase, as indicated by elemental and extracted ion analysis. Characteristic ^{31}P NMR signals are attributed to the presence of the K^+ and Br^- ions interacting with TMSHT's in toluene solution. However, even after the quantitative removal of potassium and bromide ions, new ^{31}P NMR data at low temperature (low water contents) indicate that another phenomenon takes place. NMR spectra for mixtures of zinc- and cobalt-tungstates confirm that in a nonpolar solvent two TMSHT anions join together through oxide bridges, and more NMR signals appear. Theoretical calculations show preference for certain isomeric structures.