



The Bulletin
of the
Virginia Section
AMERICAN CHEMICAL SOCIETY

SUMMER 2005 ISSUE



In a Tight Job Market, Gorilla Ph.D.'s
Have to Post-Doc at the Zoo

***** VIRGINIA SECTION NEWS *******VIRGINIA SECTION MEETINGS - FALL 2005**

- September 23** Virginia Commonwealth University, Richmond
Annual Awards Program (see below)
Local Contact Person: Dr. Sally Hunnicutt, (804) 828-8599
- October 21** Mary Baldwin College, Staunton
Dr. Matthew Neurock
"From Computational Chemistry to Catalyst and Materials Design"
Local Contact Person: Dr. Elizabeth Hairfield, (540) 887-7117
- November 18** Mary Washington College, Fredericksburg
Dr. John J. Meister
"Your Garbage = My Reactants: Trash Recycling"
Local Contact Person: Dr. Roy Gratz, (540) 654-1412
- December 2** Virginia Union University, Richmond (tentative location)
Dr. Kevin M. Dunn
"Caveman Chemistry: Hands-On Projects in Chemical Technology"
Local Contact Person: Dr. Dorothy Eseonu, (804) 257-5615

SEPTEMBER AWARDS MEETING

The September meeting of the Virginia Section will be held in Richmond at Virginia Commonwealth University on Friday, September 23, 2005. The Virginia Section will be presenting its Distinguished Service Award and Industrial Innovator Awards. Meeting details will appear in the September issue of the Bulletin. For more information, please contact Dr. Sally Hunnicutt at VCU [(804) 827-0531; sshunnic @ vcu.edu] or Virginia Section Chair Elect Dr. Dorothy Eseonu at (804) 257-5615, dneseonu @ vu.edu.

REPORT ON THE MARCH SECTION MEETING

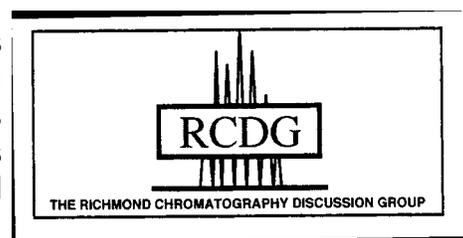
The Virginia Section met on Thursday, March 24, at Longwood University in Farmville. Dr. Fred Hawkridge of Virginia Commonwealth University spoke on "Applications of Oxidase Modified Electrodes." He was introduced by Kelly Wolcott, a senior chemistry major at Longwood University and president of their student affiliate chapter. Dr. Hawkridge's talk was preceded by a delicious dinner. Thanks to Dr. Melissa Rhoten and her colleagues and students at Longwood University for organizing this excellent meeting.

REPORT ON THE APRIL SECTION MEETING

A large gathering of about 100 persons attended the April 21 meeting at the University of Virginia. Dr. Eugene Stevens of the State University of New York at Binghamton spoke on "Green Plastics." The speaker was introduced by Brenda Goguen, a senior chemistry major at UVA. Dr. Stevens' talk was preceded by the 19th annual Poster Session that featured student research at various colleges and universities. A total of 35 posters by students from eight colleges and universities in the Section were presented (a complete list of authors and titles and abstracts of some of the papers are included in this issue of the Bulletin). Section Chair Dr. Joseph Pompano recognized fourteen outstanding senior chemistry majors from colleges and universities within the Virginia Section (the names of the recipients are listed below). The Section thanks Dr. James Demas, Ms. Susan Collins, and others at the University of Virginia who assisted with this successful meeting. Special thanks to Ms. Collins for preparing the poster program and abstracts.

RCDG

The purpose of the Richmond Chromatography Discussion Group is to promote the interests of the chromatographic and other separation sciences by expanding the awareness and capabilities of individuals from the scientific community. To meet this goal the group publishes newsletters and presents lectures at various locations in the Richmond area. Check out their website: www.rcdg.org.



OUTSTANDING CHEMISTRY GRADUATES

At the April meeting, the Virginia Section recognized graduating seniors from colleges and universities within the Section. Schools in the Virginia Section were invited to nominate senior chemistry majors for this honor. The outstanding students for the year 2005:

<u>College/University</u>	<u>Student</u>
Bridgewater College	Douglas G. Balmer
College of William & Mary	Courtney J. Hastings
Eastern Mennonite University	Richard Bryson
Hampden-Sydney College	Stefan Wiese
James Madison University	Stuart Williams
Longwood University	Danielle Zafrane
Randolph-Macon College	Sarah Elizabeth Crider
University of Mary Washington	Joanna Adams
University of Richmond	Adepeju Ligali
University of Virginia	Brenda Nicole Goguen
Virginia Commonwealth University	Steven Pitts, Farah Radwan
Virginia State University	Kathy Goodson
Virginia Union University	Cecelia Young

Poster Session and Student Awards University of Virginia - April 21, 2005



**POSTER PRESENTATIONS
UNIVERSITY OF VIRGINIA - APRIL, 2005**

Bret Adams, Dan Callahan, John Solano, Tim Caramore, John Gupton, Rob Miller and Stuart Clough, University of Richmond, **“A combination strategy for pyrrole containing alkaloids”**

Joanna Adams and Kelli Slunt, University of Mary Washington, **“Synthesis of bis-naphthalimides and studies of their interactions with DNA”**

Mithilesh Adhikari, C.W. Clemmons and K.M. Dunn, Hampden-Sydney College, **“Investigation into the intermediates and the variations of mauveine using Dunn’s method of synthesis”**

Johnese Bailey, Eytayo J. Akoda and Colleen M. Taylor, Virginia State University, **“Solvent composition effects on silica surface coordination for cobalt(II) neocuproine”**

B.T. Benedetti, S.A. Duerring and H.J. Sipe, Hampden-Sydney College, **“N-acetylcysteine [still] does not discharge the acetaminophen phenoxyl radical”**

Heath Brownlee and Serge Schreiner, Randolph-Macon College, **“Preparation and reactivity of zerovalent molybdenum-carbonyl-diphosphine complexes”**

Dan Callahan, Bret Adams, John Gupton, Rob Miller and Stuart Clough, University of Richmond, **“Suzuki type cross-coupling reactions of β -chloroenals and their application to the synthesis of biologically important coumarins”**

C.W. Clemmons and H.J. Sipe, Hampden-Sydney College, **“Alkaline ascorbate system for reducing nitroaromatics to radical anions”**

J.D. Cox and P.H. Mueller, Hampden-Sydney College, **“Preparation and evaluation of Baylis-Hillman catalysts with solid-state supports”**

Claire Crain, Kamala Payne, Jessica Richards and Vladimir Garkov, Mary Baldwin College, **“The effects of azo dyes on lactate dehydrogenase, lipoxygenase, and tyrosinase”**

Sarah Crider, Samantha Hopkins and Serge Schreiner, Randolph-Macon College, **“Synthesis, characterization and biological activity of a series of platinum(II) complexes”**

Nattawan Decharin, Amaresh R. Rajaram, Zi-Bo Li, Ying-Chuan Qin and Lin Pu, University of Virginia, **“Asymmetric phenylacetylene addition to aldehydes and trimethylsilyl cyanide addition to aldehydes catalyzed by BINOL-salen complexes”**

Lindsay Drennan, Nicole Cavadini, Jonathan Cook, Emma Goldman and Raymond Dominey, University of Richmond, **“Synthesis of a carbon dioxide reducing catalyst”**

Kevin M. Dunn, Stephen R. Diegelmann, Shea A. Duerring, Michael D. Kraemer and James L. Rock, Hampden-Sydney College, **“Investigation into the prevention of rancidity in hand crafted soap”**

Lindsay C. Fuoco, Shana Davis and Sally Hunnicutt, Virginia Commonwealth University, **“The effects of cyclodextrin on the thermal cis to trans isomerization of azobenzenes”**

Scott Geyer, Kevin Douglas, Gordon Brown and Brooks Pate, University of Virginia, **“Chirped pulse Fourier**

Kathy Goodson¹, R.M. Cicchillo², N.M. Nesbitt², D. Iwig², M. Baker², S.J. Booker² and Ralph Gatrone¹, Virginia State University¹ and Pennsylvania State University², **“Synthesis and purification of various acyl-ACP derivatives”**

Daryl A. Guthrie and John D. Thoburn, Randolph-Macon College, **“Design of chromophore for chiroptical molecular switches based on dithiocarbamate-iminodithiolane interconversion”**

Charlotte E. Hinkle, Pamela L. Crum, Brian Dian, Hyun S. Yoo and Brooks H. Pate, University of Virginia, **“Dynamics of gas and solution phase acid dimers”**

Kwo Wei Ho and David Cafiso, University of Virginia, **“The effect of detergent micelle environments on the conformation of BtuB outer-membrane protein”**

Samantha L. Hopkins and Serge Schreiner, Randolph-Macon College, **“Synthesis and characterization of water-soluble diphosphine ligands and their platinum complexes”**

Richard B. Keithley, Sarah E.G. Porter and Sarah C. Rutan, Virginia Commonwealth University, **“Characterization of potential drug interactions between dextromethorphan, fluoxetine, and PMMA”**

K.M Knott, S.L. Pitts, Y. Qu, and N.P. Farrell, Virginia Commonwealth University, **“Platinum recovery: an inherently dangerous procedure for only the most dispensable of lab students”**

Nick Lauerman, John Solano, John Gupton, Rob Miller and Stuart Clough, University of Richmond, **“Microwave accelerated reactions for the formation of pyrroles from vinamidinium salts”**

Adepeju Ligali, Matthew Rooberts, Heather Petruzzi, Tsegahiwot Belachew, Seann Mulcahy, Ivanka Kamenova, Stuart Clough, John Gupton and Robert Miller, University of Richmond, **“Conversion of carboxylic acids to dimethylaminomethyl esters”**

Yunqing Lin and W. Dean Harman, University of Virginia, **“Dihapto-coordinated carbonyl complexes and their role in chemistry”**

My-Linh Nguyen, Kevin Welch and W. Dean Harman, University of Virginia, **“Synthesis and characterization of $Tp(W(NO)(PMe_3)(\eta^2-4H-pyran-4-one))$ ”**

Matthew Olsen and W. Dean Harman, University of Virginia, **“Synthesis and reactivity of 2,5-dimethylfuran complexes”**

Tim Reichart, Chris Mocella and W. Dean Harman, University of Virginia, **“The reactivity of naphthalene facilitated by an unusually π -basic molybdenum(0) metal fragment”**

H.S. Sanders, D.K. Williams, Jr., J. Rock and P.H. Mueller, Hampden-Sydney College, **“Determining the effects of tethered urea groups on imidazole-catalyzed Baylis-Hillman reactions”**

Ted V. Shaner¹, Gregory So Long² and April D. Marchetti¹, Randolph-Macon College¹ and Los Alamos National Laboratory², **“Copolymerization of heteronorborenes with styrene and acrylates via copper-mediated ATRP”**

Elizabeth M. Spero and Serge Schreiner, Randolph- Macon College, **“Preparation of a synthetic receptor for the age determination of cognac”**

Caleb Strepka¹, Gregory S. Long² and April D. Marchetti¹, Randolph-Macon College¹ and Los Alamos National Laboratory², **"Investigation of palladium-initiated insertion polymerization from inorganic surfaces"**

Yogesh Surendranath, Hill Harman and W. Dean Harman, University of Virginia, **"Synthesis and reactivity of η^2 -diazine tungsten(0) complexes"**

Paul Walsh and Charles Sharpless, University of Mary Washington, **"Photochemistry of humic substances: quantum yields of singlet oxygen"**

QUESTIONS FROM THE PAST

This question was asked in the April Bulletin: The Nominating Committee for the Virginia Section presented a slate of officers that included Robert Timberlake Kemp, Jr. for Chairman, Franklin D. Kizer for Chairman-Elect, and Carl Trindle for Vice-Chairman. What year was that? **The year was 1975.**

A new question from the past: April was a special month for the Virginia Section. Two meetings were held. The speaker for the Richmond meeting was a woman chemist, Florence E. Wall, who spoke on "Cosmetics as a Field of Chemical Research." Later that month in Williamsburg there was a joint meeting with the Hampton Roads Section. Speakers were R.C. Herman of the Johns Hopkins University who spoke on "The Origin of the Elements," and Rev. A.E. Acey of Portsmouth who treated the subject "Noblesse Oblige" with deftness and humor. The same month saw the Section sponsor a Seminar on Research and Development that was planned and directed by the Virginia-Carolina Chemical Corporation. The panel of speakers included Dr. S.S. Negus, Dr. Allan Gwathmey, Dr. Lauren B. Hitchcock, Dr. Milton Harris, and Dr. John Weiss. The concluding address was by the Hon. Colgate W. Darden, President of the University of Virginia and former Governor of the Commonwealth. He spoke on "Scientific Research and Our American Way of Life." **In what year was this month of memorable Section activities?**

DRAWING ON COVER

The cartoon on the cover of this issue of the Bulletin was done by Eddie Thomas, Councilor for the Virginia Section. Drawing is one of Eddie's hobbies. He has done cartoons for the covers of twelve issues of the Bulletin. Eddie served as Chair of the Virginia Section in 1988 and received the Distinguished Service Award in 1993. He has been a Section Councilor since 1995 and is a member of the national ACS Membership Affairs Committee and is the MAC liaison to the Committee on Constitution & Bylaws. He is retired from R&D at Philip Morris USA.

GRANTS FOR K-12 SCIENCE PROJECTS

The Virginia Section is soliciting proposals for grants to support school science projects in grades K through 12. The \$50 to \$500 grants will be provided to teachers in the Virginia Section for the purchase of materials and supplies. To apply for support, request an application form from Mr. Ryan Warren, 304 N. Sheppard Street, Richmond, VA 23221; (804) 342-1323; warrencr @ vcu.edu. Or complete an application on-line by accessing the Virginia Section website at <http://membership.acs.org/VVA/grants.htm>.

VIRGINIA SECTION WEBSITE

Information on Virginia Section meetings, copies of the Bulletin, and much more can be found on the Virginia Section Website. It can be accessed via <http://membership.acs.org/VVA/>. There are links to a variety of other ACS and chemistry sites. Dr. Ann Sullivan is the Webmaster. Contact her at asullivan@reynolds.edu.

FIFTY-YEAR MEMBERS OF THE ACS

Congratulations to these Section members, each of whom has been a member of the American Chemical Society for 50 years:

Basil C. Doumas	Fredericksburg
David A. Hazlehurst	Richmond
Robert Martin	Earlysville
Thomas S. Osdene	Richmond
Robert Carryll Parsons	Richmond
R. Cynthia Pruett	Manassas
W. H. Starnes	Williamsburg

NEW MEMBERS OF THE VIRGINIA SECTION

We welcome these new members of the Virginia Section:

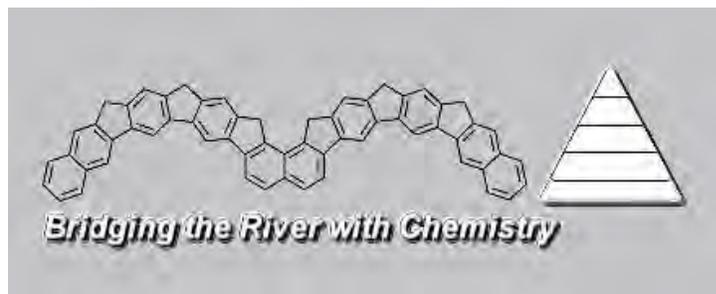
VICTOR ABD ELSAYED	AL D AMRELLE	JUDIT BARTALIS	KIMBERLEY C BASSETT
CHARLES J BRANDENBURG	MILTON L BROWN	WEIDONG CAO	FREDERIC L CINER
PHILIP A EGAN	ROBIN A FELDER	GEORGE C FOHL	MALISSA HELDRETH
WANGQI HOU	TERRY W HUDSON	MARTA ANDREA JAKAB	CLINTON D JONES
JACOB L JORDAN	GAJANAN S JOSHI	AMAR KALIDINDI	SHIV N KHANNA
DMITRI K KLIMOV	CHANDRAVELKRISHNASAMY	KELLY M LANGFORD	MICHAEL B LAWRENCE
CARLA H LEE	BRENT A MANTOOTH	MANUEL MARQUEZ	KARLA E MARZ
CHERYL L MEANS	CHRISTAL M MILLER	VICTOR MOROZOV	MELISSA C RHOTEN
KEITH RIPPEL	JOSEPH E ROEHL	BENJAMIN ROTHERMEL	JOSEPH J SAADY
JESSE S SABATINI	CHANTEL L SABUS	SCOTT THOMAS SANDHOLM	PAUL H SARTORI
BENJAMIN R SCHROEDER	SHERRY SHERMAN	GENE A STARK	DEBRA S STRICKLAND
QIN SUN	JENNIFER TRENT	LAKSHMINIRANJAN VANIMIREDDY	JIHANG WANG
YOUNG WANG	KERMIT R WAY	JIAN WEN	CHRISTINE A WINSCHER
YUNZHI XIAO	IBRAHIM H ZGANI	YM ZHAI	WENYI ZHAO
MOLLY A ZIGLER			

HOSPITALITY COMMITTEE

The Virginia Section Hospitality Committee sends a letter of welcome to each new member of the Virginia Section. A new member who brings his or her letter to a Section meeting receives a free dinner. The Chair of the Hospitality Committee is Mrs. Phyllis James. She can be contacted at (804) 652-6582; [jamesp @ wyeth.com](mailto:jamesp@wyeth.com).

SOUTHEAST/SOUTHWEST JOINT MEETING

The joint Southeast/Southwest regional meeting will be held at the Peabody Hotel in Memphis, Tennessee, November 1-4, 2005. The meeting program will include many special events, symposia and workshops. Abstracts for symposia, general sessions, and poster sessions can be submitted through the online abstract system .



Examples of symposium topics include:

- a. Innovations in the Teaching of Chemistry (CHED)
- b. Guided Inquiry in the Chemistry Curriculum (CHED)
- c. Computational Chemistry
- d. Environmental Health and Safety
- e. Advances in Chiroptical Methods: A New Resource for Chiral Chemistry
- f. AFM and STM
- g. Chemistry and the Law
- h. Nanomaterials and Composites: Synthesis, Properties and Applications
- i. Developments in NMR Spectroscopy
- j. NMR and Structural Biology
- k. Biomedical Applications of Polymers
- l. Spectroscopy of Matrix-isolated Species
- m. Frontiers in Nucleic Acid Chemistry
- n. Cope Award Symposium
- o. Biosensors
- p. Bioactive Lipids

There will be workshops on ACS Insurance, Hygiene and Safety, and How to Start a Co-op program. The ACS Office of Career Services will present workshops and hold a Regional Employment Clearinghouse onsite.

Other special events will include a "Meeting in Miniature" for undergraduate student presentations and posters. (Papers must be submitted through the online abstract system .) A Graduate School Fair will be held in conjunction with the undergraduate meeting.

The program will also include the Southern Chemist Award Address, and the SE and SW Industrial Innovations Award presentations.

An exhibition will take place during the middle two days of the meeting, Wednesday and Thursday, November 2nd and 3rd, and the Graduate School Fair will be held on Friday, November 4.

Richard Peterson is the General Chair, Roger Lloyd is Associate Chair, Henry Kurtz is the Program Chair, and Bill McLaughlin is Exhibits Chair. Full information on the meeting can be found at www.chem.memphis.edu/acs/seswrm.html.

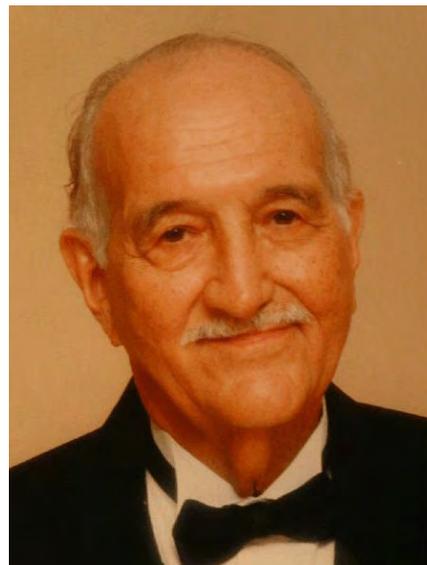
WORDS OF WISDOM FOR THE SUMMER: "If you want to be as good as your word, don't say a thing"

IN MEMORIAM

James Vincent Quagliano 1915 – 2005

Dr. James (Jim) Vincent Quagliano, noted chemical educator and a member of the American Chemical Society for over 50 years, died on May 12. Jim received his Bachelor's and Master's Degrees in Chemistry at Brooklyn Polytechnic (working with Professor Roland Ward), graduating in 1940. His first teaching assignment was as Instructor of Chemistry at Villanova College from 1940 to 1943. Jim's love of chemistry and teaching inspired him to continue his studies at the University of Illinois, where he received his Doctorate degree in Inorganic Chemistry (working with Professor John Bailar) in 1946.

After receiving his Ph.D., he held teaching positions at the University of Notre Dame (Associate Professor, 1948-1958), Florida State University (Professor, 1958-1975), Auburn University (Hudson Professor of Chemistry, 1975-80), and the College of William and Mary (Visiting Professor, 1980-1981). After retirement, he taught freshman chemistry classes at Virginia Commonwealth University. For over 50 years, his unassuming teaching approach and sheer fascination with chemistry inspired students to love a subject which they had previously feared; he became known affectionately – and simply – as “Dr. Q.”



Jim Quagliano was the recipient of numerous awards and honors during his academic career, including the Award of Honor of the University of Notre Dame (1965), the Fellowship of the American Association for the Advancement of Science (1972), and the Florida Section Award of the American Chemical Society (1975). He received two Fulbright Fellowships – one at Bologna, Italy (1956) and one at Roma, Italy (1966). He was a leader in the field of coordination chemistry. He introduced the use of infrared spectroscopy for the qualitative analysis, structural characterization, and the elucidation of metal-to-ligand bonding in metal complexes (1953–1960, 22 publications).

In particular, he was the first to employ the now universally adopted KBr pressed-disk technique for the infrared spectra of inorganic compounds. Also, he developed and studied a novel class of coordination compounds, in which positively-charged organic ligands were bound to (positively charged) transition metal ions (1964-1974, 10 publications). In some of these compounds—such as the complex of Ni^{2+} with $\text{NH}_2\text{N}^+(\text{CH}_3)_3$ —the cationic metal center and the positively charged atom of the ligand were separated by only one atom, showing that the tendency to form the coordinate bond could overcome the electrostatic repulsion.

Dr. Quagliano was the author of over 70 scientific articles, three chapters in the “International Encyclopedia of Chemistry” (1971), two college-level textbooks: “Chemistry” (3 editions, 1958, 1963, and 1969, translated into Italian, Portuguese and Japanese) and “Coordination Chemistry” (1969), and a high-school textbook: “Chemistry—A Humanistic Approach” (1975). Jim's wife Lidia, also an Inorganic Chemist, worked with him as co-author on several of the research articles and the two more recent textbooks.

Jim Quagliano is survived by his wife Lidia, who is a Chemistry Professor at Virginia Commonwealth University, three children (one of whom is a Physical Chemist), three grandchildren, and a younger sister. On July 3, Jim and Lidia would have celebrated their 44th wedding anniversary.

ABSTRACTS OF POSTER PRESENTATIONS APRIL 15, 2004 - UNIVERSITY OF VIRGINIA

A Combination Strategy for Pyrrole Containing Alkaloids, Bret Adams, Dan Callahan, John Solano, Nick Lauerman, Tim Caramore John Gupton, Rob Miller, and Stuart Clough, Department of Chemistry, University of Richmond, Richmond, VA 23173.

Our previous efforts involving the use of 2,3-diaryl-3-chloroenals for the synthesis of bioactive marine alkaloids has recently culminated in the relay synthesis of bioactive marine alkaloids Lukianol A, Lamellarin O and Ningalin B. Current work in our lab focuses on an alternative strategy, which involves the use of symmetrical vinamidinium salts for the preparation of 2-carboalkoxy-4-arylpyrroles, which can be further functionalized by electrophilic substitution followed by halogenation and Suzuki type cross-coupling chemistry. The resulting products of such a sequence become key synthons for the growing family of pyrrole containing marine natural products. Ongoing work in this area will be presented.

Synthesis of Bis-naphthalimides and Studies of Their Interactions with DNA, Joanna Adams and Kelli Slunt. Department of Chemistry, University of Mary Washington, Fredericksburg VA

Compounds capable of intercalation into DNA have been studied in an effort to inhibit the relaxing capabilities of topoisomerase II (topo II) during the transcription process of DNA in tumor cells, leading to cell death. Five bis-naphthalimides were synthesized from naphthalic anhydride and amines, which serve as the linker chains connecting the two naphthalimide chromophores. Proton NMR and IR spectra were used to confirm the structure of the compounds. UV-Vis studies with calf thymus DNA, DNA unwinding studies using topo I as well as topo II drug screening studies were also performed on each drug, in an effort to determine the intercalative capabilities and mechanism of intercalation of each drug. Yeast studies were also performed to examine the cytotoxicity of the bis-naphthalimides. Compounds one through four exhibited the intercalative activity while difficulties with dissolving compound five in solution prevented an accurate analysis.

Investigation into the Intermediates and the Variations of Mauveine Using Dunn's Method of Synthesis, Mithilesh Adhikari, C.W. Clemmons, and K.M. Dunn, Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, VA 23943

Intermediates of the o-toluidine dye has the same properties of Perkins's mauveine, using Dunn's method were isolated and characterized using UV-Vis spectroscopy, TLC, and gel electrophoresis. Two intermediates were isolated: the first was a short-lived brown and the second a positively charged blue that gradually turned purple. Similar characterizations were performed on Dunn's purples synthesized from various anilines. As predicted from the structure given by Otto Meth-Cohn, in addition to aniline, only the ortho- and meta-substituted anilines yielded purple dyes. The results were consistent with that of Perkins's mauveine: each dye had maximum absorbance peak in the range that is expected of mauveine (538 nm – 560 nm); TLC results showed each dye had distinct but different purple color; the gel electrophoresis confirmed that the dyes were cations, and when used to dye test fabrics, each dye showed best effect on silk.

Suzuki Type Cross-coupling Reactions of β -Chloroenals and Their Application to the Synthesis of Biologically Important Coumarins, Dan Callahan, Bret Adams, John Gupton, Rob Miller, and Stuart Clough, Department of Chemistry, University of Richmond, Richmond, VA 23173.

α -Chloroenals are readily accessible substances and are efficient precursors for a variety of heterocyclic compounds. We are currently examining the Suzuki type cross-coupling reactions of such compounds with arylboronic acids in which case α,α -diaryl substituted enals are produced with control of stereochemistry. The oxidation of these enals to the corresponding acid and subsequent LTA oxidative lactonization to the respective coumarins will be described.

Solvent Composition Effects on Silica Surface Coordination for Cobalt(II) Neocuproine, Johnese Bailey, Eytayo J. Akoda, and Colleen M. Taylor, The Department of Chemistry and Physics, Virginia State University, Petersburg, Virginia 23806

Surface coordinated complexes are important in heterogeneous transition metal catalyst systems. Synthesis techniques for these heterogeneous catalysts can dramatically affect the identity and/or homogeneity of active surface species. Recent work has elucidated a useful silica surface probe formed from octahedral $[\text{Co}(\text{neo})(\text{H}_2\text{O})_4]^{2+}$ (neo = neocuproine). This pink octahedral solution species binds to silica gel surfaces to form an exclusively blue tetrahedral surface adduct. Further work has provided information on the steric effects that promote surface coordination in purely tetrahedral symmetry. In this latest work, grafting studies were conducted in aqueous solutions. We have noted a decrease in surface affinity as a function of increased methanol content in grafting solutions. Decreased affinity for the surface is thought to arise from the preferential solvation of the neocuproine complex by bulk methanol solution rather than at the silica surface. We are therefore studying the grafting of this surface species in differing MeOH:H₂O ratios and extending the study to the grafting cobalt(II) complexes of bathocuproine and 6,6-dimethyl-2,2-dipyridyl. This study will contribute to the understanding of factors effecting surface coordination in transition metal based heterogeneous materials.

N-Acetylcysteine [Still] Does Not Discharge the Acetaminophen Phenoxy Radical, B.T. Benedetti, S.A. Duerring, and H. J. Sipe, Jr., Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, VA 23943.

Acetaminophen (ACAP) is commonly used as a painkiller, but overdoses can cause liver hepatotoxicity. N-acetylcysteine (NAC) is a known antidote for acetaminophen intoxication. Three mechanisms have been proposed for the antidote: (1) increased glutathione production; (2) inhibition of liver cytochrome P-450 enzymes that metabolize ACAP to a toxic form; and (3) depletion of the acetaminophen toxic intermediate. Previous investigators observed highly reactive phenoxy free radicals formed by enzymatic peroxidation of ACAP. Direct ESR observation of these short-lived radicals used fast flow ESR techniques in which solutions of reactants were mixed at a flat cell in the ESR cavity. Because ACAP phenoxy radicals were observed during ACAP metabolism, we hypothesized that NAC antidotal action was likely mechanism (3) –discharge of $\text{ACAP}\cdot$ by hydrogen atom transfer from NAC to $\text{ACAP}\cdot$. We observed the ACAP phenoxy radical by mixing a solution of 20mM ACAP and 25mM H₂O₂ with a solution of 0.110mM hemoglobin in a Wilmad mixing flat cell at a total flow rate of 40 mL/min. We studied the $\text{ACAP}\cdot$ concentration as a function of NAC from 0mM to 200mM and find suppression (0.8X) of $[\text{ACAP}\cdot]$ at low [NAC] but significant enhancement (2.4X) of $[\text{ACAP}\cdot]$ at 100mM [NAC] and lesser enhancement at higher [NAC]. These results suggest that NAC may discharge $\text{ACAP}\cdot$ at low concentrations but is involved in the radical formation at higher concentrations.

Synthesis, characterization and biological activity of a series of platinum(II) complexes, Sarah Crider, Samantha Hopkins and Serge Schreiner, Department of Chemistry, Randolph-Macon College, Ashland, VA

A series of mononuclear platinum complexes with the diphosphine ligands 1,2-bis(bis(hydroxymethyl)phosphino)ethane (DHMPE), 1,2-bis(bis(hydroxybutyl)phosphino)ethane (DHBuPE), 1,2-bis(bis(hydroxypentyl)phosphino)ethane (DHPePE), and 1,2-bis(bis(hydroxyhexyl)phosphino)ethane (DHHePE) were synthesized and characterized by multinuclear NMR techniques. NMR data support the formulation of these complexes as square-planar, mono- and bis-chelated platinum(II) complexes of the type $[\text{PtL}_2]\text{Cl}_2$ and $[\text{PtLCl}_2]$, (L = diphosphine ligand). The relative water-solubility of these complexes could be adjusted by modifying the length of the hydrocarbon chain on the diphosphine ligand. Bacterial inhibition studies show that these complexes are biologically active against gram-positive and gram-negative bacteria. Comparative tests were undertaken to study the ability of these complexes to bind 5'-guanosine monophosphate (5'-GMP) and DNA. Preliminary results from UV/vis spectroscopic studies and ¹H NMR studies suggest that some of these complexes are capable of binding 5'-GMP and DNA.

Preparation and Reactivity of Zerovalent Molybdenum-Carbonyl-Diphosphine Complexes, Heath Brownlee and Serge Schreiner, Department of Chemistry, Randolph-Macon College, Ashland, VA 23005

Decarbonylation of molybdenum hexacarbonyl in refluxing decane in the presence of the bulky diphosphine ligands, *bis*(dicyclohexylphosphino)methane (dcpm) or *bis*(dicyclohexylphosphino)ethane (dcpe) yielded the mononuclear, singly chelating complexes, Mo(CO)₄(dcpm) (**1**) and Mo(CO)₄(dcpe) (**2**) in about 50% yield. These complexes appear to be similar in structure to previously reported molybdenum-dppm (*bis*-diphenylphosphino)methane and molybdenum-dppe (*bis*(diphenylphosphino)ethane) complexes. Further reaction of complex (**1**) with one mole equivalent of dcpm yielded a dinuclear, bridging complex tentatively formulated as Mo₂(CO)₄(μ-dcpm)₂(η²-dcpm)₂ (**3**). Complexes (**1**) and (**2**) were also reacted with strong acids in an attempt to generate molybdenum-hydrido complexes. The results of these reactions will be discussed. Reaction of (**3**) with carbon monoxide or dioxygen resulted in the fragmentation of the dinuclear complex..

Preparation and Evaluation of Baylis-Hillman Catalyts with Solid-State Supports, J.D. Cox and P.H. Mueller, Department of Chemistry, Hampden-Sydney College, Virginia 23943

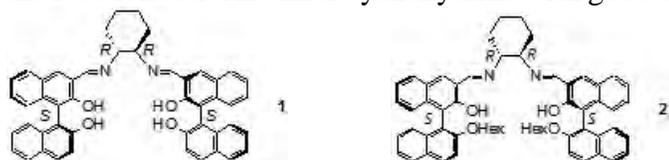
Evidence suggests that a Baylis-Hillman reaction catalyst, 1-(3-aminopropyl)imidazole, was attached to 3-(Glycidoxy)propyl-functionalized silica gel with the influence of lithium trifluoromethanesulfonate. This system successfully catalyzed the Baylis-Hillman reaction of *p*-nitrobenzaldehyde with methyl vinyl ketone but not with methylacrylate. Also reported, the unsuccessful attempts to attach 1,5,7-triazabicyclo[4.4.0]dec-5-ene, 3-(Isocyanato)propyl-functionalized silica gel, and Isocyanate, polymer bound to 3-(Glycidoxy)propyl-functionalized silica gel. Polystyrene-bound 1,3,4,6,7,8-Hexahydro-2H-pyrimido(1,2-*a*)pyrimidine (Aldrich) was found not to catalyze the Baylis-Hillman reaction.

Alkaline Ascorbate System for Reducing Nitroaromatics to Radical Anions, An ESR Study. C.W. Clemmons and H. J. Sipe, Jr., Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, VA 23943.

Aromatic radical anions are often produced by reduction with alkali metals, by electrochemical reduction, or sometimes by photochemical reactions. Mason and coworkers reported ESR studies of nitro-substituted drug molecules reduced to radical anions by ascorbate solutions in anaerobic solutions at high pH. We reproduced the Mason, *et al.* ESR studies of metronidazole and nitrofurantoin, and then extended the ascorbate reduction method to study the ESR spectra of representative nitroaromatic radical anions: *p*-nitroacetophenone, and *o*-, *m*-, and *p*-nitrobenzaldehyde. The ESR spectra of metronidazole and nitrofurantoin radical anions are in agreement with the published literature. Assignment of hyperfine coupling constants for the representative nitroaromatic radical anions are reported and compared with published values where available.

Asymmetric Phenylacetylene Addition to Aldehydes and Trimethylsilyl Cyanide Addition to Aldehydes Catalyzed by BINOL-Salen Complexes, Nattawan Decharin, Zi-Bo Li, Amaresh R. Rajaram, Ying-Chuan Qin and Lin Pu, Department of Chemistry, University of Virginia, Charlottesville VA 22904

Previously the *bis*binaphthyl compound **1** in combination with Me₂Zn was found to catalyze the addition of alkynes to aromatic aldehydes with high enantioselectivity (86-97% ee). This ligand was modified to study the factors that influence its catalytic properties. The results showed that the chiralities of both the BINOL units and the carbon centers are very important. The absence of the carbon center chirality gave low enantioselectivity. The use of compound **1** and its derivatives in the asymmetric addition of trimethylsilyl cyanide to benzaldehyde was also examined. Compound **2** in combination with Ti(O^{*i*}Pr)₄ was found to catalyze the reaction to form chiral cyanohydrins with good enantioselectivity (75-85% ee) at room temperature.



The Effects of Azo Dyes on Lactate Dehydrogenase, Lipoxygenase, and Tyrosinase, Claire Crain, Kamala Payne, Jessica Richards and Vladimir Garkov, Department of Chemistry, Mary Baldwin College, Staunton, VA 24401

The purpose of this study was to measure enzyme activity in the presence of the azo dyes, amaranth, allura red, and tartrazine. Enzyme kinetics methods were used to measure the enzyme activity. It was hypothesized that there would be a difference in activity in the presence of the dyes. Only 1.6×10^{-5} M of allura red on lactate dehydrogenase had a significant increase of activity; supporting the hypothesis.

Investigation into the Prevention of Rancidity in Hand Crafted Soap, Stephen R. Diegelmann, Shea A. Duerring, Michael D. Kraemer, James L. Rock, and Kevin Dunn, Department of Chemistry, Hampden-Sydney College, Hampden-Sydney VA 23943

The prevention of rancidity in hand crafted soap created using the cold-process method was studied in order to determine an effective method to prevent the formation of so-called "dreaded orange spots." The spots have been previously linked to oxidation of the soap so various methods were tested to prevent soap oxidation. These methods included the addition of various antioxidants and ligands to the soap in an effort to extend the time before the orange spots formed. Different mixing methods to prevent the presence of unsaponified oil in the soap and the use of oils not containing double bonds were also tested as ways to prevent oxidation. The combination of a fifteen minute shake time with BHT and Sodium Citrate added is the most effective method of orange spot prevention tested thus far. Further testing of other combinations of antioxidants with ligands is currently in progress. Rosemary Oleoresin Extract and Sodium Citrate are showing great promise.

Computer Interfacing of Instrumentation for Measuring Oxygen Diffusion Coefficients in Polymer Films, Chi-Linh Do-Thanh, Daniel L. McCauley, M. Cuber, and James N. Demas, Department of Chemistry, University of Virginia, Charlottesville, VA 22904

The diffusion coefficient (D) is an important parameter for polymer applications, such as luminescence-based oxygen sensors. For example, in oxygen sensors the diffusion coefficient determines the response time of the sensor. For measuring oxygen Ds, an instrument was built that monitors the time dependence of the emission intensity of a metal complex in a polymer film following a step change in the gas phase oxygen concentration. From the time dependence of the emission intensity, the luminescence quenching properties, and the film thickness, D can be determined. The main goal is to automate the entire process from reading the intensity to calculating D. A computer program written in the graphically interfacing language LabVIEW is used to measure oxygen diffusion in polymers by luminescence quenching. The instrument uses a blue LED to excite the sample, an electronically controlled shutter to turn the source on and off to minimize photochemistry, photomultiplier tubes (PMTs) to measure the emission intensities, and an electronic valve for switching the oxygen concentration over the sample. The program controls the operation of the instrument and reads and analyzes the data. The resulting intensity versus time profile is fitted by nonlinear least squares to an appropriate diffusion model using a Mathcad program working through LabVIEW, from which the diffusion coefficient for the polymer film can be obtained. An instrument description and results will be presented.

Synthesis of a Carbon Dioxide Reducing Catalyst, Lindsay Drennan, Nicole Cavadini, Jonathon Cook, Emma Goldman and Raymond Dominey, Department of Chemistry, University of Richmond

There is an abundance of carbon dioxide in the atmosphere, which is a potential starting material for alternative fuel sources. Hence it would be useful to find a way to efficiently reduce carbon dioxide. The single electron reduction of carbon dioxide is the most basic step in its conversion to other organic products. Our project involves synthesizing a series of copper complexes with open α, α -diimine ligands and ascertaining if these would be efficient electrocatalysts for the electrocatalytic reduction of carbon dioxide. Our work thus far has focused on the synthesis of the disubstituted pyridine ligands required to make the copper electrocatalyst.

The Effects of Cyclodextrin on the Thermal Cis to Trans Isomerization of Azobenzenes , Lindsay C. Fuoco, Shana Davis and Sally Hunnicutt, Department of Chemistry, Virginia Commonwealth University, Richmond, VA.

We have investigated the effect of cyclodextrins on the thermal cis-to-trans isomerization of 4,4'-dimethylaminophenyl-azobenzoic acid sodium salt (p-methyl red). When irradiated with light, azobenzenes switch from the thermodynamically more stable trans to the cis isomer, which quickly returns to the trans isomer. This property of azobenzenes makes them possible candidates as molecular switches or image storage devices. UV-Vis spectra show that β -cyclodextrin interacts more strongly with p-methyl red compared to the α - and γ -cyclodextrins. Chemometric analysis of the UV-Vis spectra resolves two distinct species for p-methyl red complexes with α - and γ -cyclodextrin and three species for complexes with β -cyclodextrin. The cis-trans isomerization rate constant for p-methyl red is lower when complexed with α , γ and β -cyclodextrin. These results, along with theoretical modeling, suggest that p-methyl red may form 1:1 complexes with α - and γ -cyclodextrins and may form inclusion complexes with β -cyclodextrin.

Chirped Pulse Fourier Transform Microwave Spectrometer Design, Scott Geyer, Kevin Douglass, Gordon Brown, Brian Dian, and Brooks Pate, Department of Chemistry, University of Virginia, Charlottesville VA 22904

An 11 GHz broadband Chirped Pulse Fourier Transform Microwave Spectrometer (CP-FTMW) has been developed that increases the microwave bandwidth measured from a single light pulse by 5,500 over traditional narrow band cavity designs. This technique also gives accurate peak intensity information and a way to monitor the entire spectrum while varying parameters. It is compatible with a multi-pass IR laser excitation system for IR-MW double resonance experiments. This new technique was made possible through the use of an arbitrary waveform generator (AWG) which is capable of creating user defined linear sweep (chirped) pulses. For 11 GHz excitation, the AWG creates a chirped pulse that sweeps through 1.375 GHz in 1 s. Multiple frequency doubling steps increase the bandwidth by a factor of eight to give the 11 GHz linear sweep. This pulse provides excitation through fast adiabatic passage with a signal that is inversely proportional to the square root of the bandwidth. In addition to creating linear sweep pulses, the arbitrary waveform generator can easily create pulse sequences for MW-MW and IR-MW-MW double and triple resonance experiments to probe and decouple excited states. New techniques such as 2D MW experiments to efficiently decouple the eigenstates are being investigated. Further work on the system includes ways to increase the signal to noise to further decrease data acquisition time, such as a multi nozzle system to increase the molecular signal.

Dynamics of Gas and Solution Phase Acid Dimers, Charlotte E. Hinkle, Pamela L. Crum, Brian Dian, Hyun S. Yoo, and Brooks H. Pate. Department of Chemistry, University of Virginia, Charlottesville, VA 22904

Using Fourier transform infrared spectroscopy and our time domain ultra-fast infrared spectrometer located in the CAMOS Ultrafast Laser Facility at the University of Virginia we are examining vibrational dynamics of acid dimers. Acid dimers are useful models of complex biological systems. We are currently studying formic acid and trifluoroacetic acid dimers. Gas phase FTIR, and gas and solution phase time-domain ultra-fast experiments have been performed. Using FTIR, spectra are taken in 20° increments from 25 to 160°C. Trifluoroacetic acid has a CO stretch with a smooth peak at 1785 cm⁻¹ at 25° which shifts to 1830 cm⁻¹ as the temperature is increased. This forms an isosbestic point in the data and faint P, Q, R branch splitting is visible in the 1830 cm⁻¹ peak. As the gas is heated a free OH peak grows in at 3585 cm⁻¹. A redshifted, broad hydride stretch which is visible between 2400 and 3450 cm⁻¹ diminishes as the temperature is increased. Using our time-domain ultra-fast laser technique, energy is put into this hydride stretch at 2972 or 2953 cm⁻¹; we then study the effects this energy has on the system and the dimer dissociation process. Using our technique we hope to produce a mechanism for the acid dimer to monomer transition and learn about the dynamics of these molecules. Solution phase molecules show rapid relaxation into the lower energy state, while gas phase molecules offer a greater window to understanding the dimer dissociation process. Future work involves deuterated dimers to determine an intermediate structure.

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CAN YOU IDENTIFY THIS PERSON?

This individual was awarded the Section's Distinguished Service Award for High School Chemistry Teaching in the year 1952. She attended Madison College and held a B.S. degree from the University of Virginia. At the time of her Award, she was teaching science in Dayton, Virginia. She had also taught at the Pleasant Hill School and at Warren County High School. She was a charter member of the Virginia Junior Academy of Science. Her students excelled in the Junior Academy and in competitions such as the National and Virginia Science Talent Search.

The "Mystery person" shown in the April Bulletin was **Robert T. Kemp, Jr.** Bob was the Chair of the Virginia Section in 1975.



