

THE NUCLEUS

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Monthly Meeting

*A Medicinal Chemistry Symposium on
Emerging Treatments for CNS Disorders*

Summer Scholar Report

By John J. Sirois and Dr. Donald Boerth

Book Review

By Heather E. Burks

Education Night Awards

May 13, 2010

Book Review

Gold Chemistry. Applications and Future Directions in the Life Sciences. Edited by Fabian Mohr (Wiley-Interscience, 2009) 408 pp., ISBN: 9783527320868 \$215

Reviewed by Heather E. Burks, Novartis Institutes of Biomedical Research, Inc., Cambridge, MA

Gold has existed for centuries; however, the importance of this metal in chemistry has become evident with the exponential increase in the number of gold-centered publications over the last three decades. In almost all of the chemistry journals, at least one research article on gold chemistry is published in every issue. The chemistry of this element encompasses all disciplines of chemistry, from organic, inorganic, physical, and theoretical to materials sciences and medicine. "Gold Chemistry. Applications and Future Directions in the Life Sciences," edited by Fabian Mohr, summarizes the most active areas of research in gold chemistry. Mohr has organized the book into two sections, each containing four chapters. The first section is devoted to the new chemistry of gold, while the second section covers the current and future applications of gold.

Chapter one, written by John P. Fackler, Jr., focuses on gold(I) nitrogen coordination complexes. Gold is a soft metal and typically prefers soft ligands like phosphorus and sulfur over hard ligands which are nitrogen- or oxygen-based. The authors outline the preparation of mono-, poly-, and heteronuclear gold(I) complexes with amidinate, pyrazolate, and guanidinate ligands. An advantage of preparing the gold(I) complexes with nitrogen-ligands which are in poly- or heteronuclear complexes is that the metal ions are in closer proximity than with traditional ligands on gold. Gold-gold interactions are required for luminescence. Gold(I)-nitrogen coordination complexes are used in the preparation of luminescent materials, which is one of many applications discussed.

In the second chapter, Maria Agostina Cinelli covers the chemistry of gold(III) complexes with nitrogen

and oxygen ligands. An expansive discussion about the preparation of gold(III) coordination complexes with neutral, anionic, and multidentate ligands is included. The application of these complexes is medically based. Several gold(III) complexes with nitrogen ligands are active against human cancer cell lines that are resistant or sensitive to *cis*-platin. The biological activities of various gold(III) complexes, some of which are more cytotoxic than current drugs, are integrated throughout the chapter. The synthesis of gold(III) complexes with oxygen ligands concludes the chapter. The application of gold(III)-oxygen complexes is also rooted in medicinal chemistry; however, these complexes may also be used in olefin oxidation.

Chapter three, written by M. Laguna and co-workers, encompasses the preparation of pentafluorophenyl gold complexes. The pentafluorophenyl ligand is important in gold chemistry because it imparts a degree of stabilization to gold. The complex is usually bound through the *ipso*-carbon of the pentafluorophenyl ligand. This ligand is also important for crystallinity. Several gold complexes have been prepared that are only stable with the pentafluorophenyl ligand. The chapter covers the preparation of pentafluorophenyl gold complexes with the oxidation states of (I), (II), and (III) with various ligands. Heteronuclear-gold complexes are also described. Pentafluorophenyl gold complexes have been used in liquid crystals, gold clusters, luminescent and vapochromic materials, as well as in volatile organic compound detectors.

In the fourth chapter, Peter Schwertfeger and Matthias Lein discuss the theoretical chemistry of gold. A concise yet comprehensive explanation of the relativistic effects on gold is provided. Calculations on atomic gold, gold clusters, inorganic, and organo-

continued on page 4

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Cover: *Pictured at Education Night receiving the Simmons College Award for the top score in the Fifty-First Annual Avery Ashdown Exam is James Lim of Phillips Academy Andover. He is receiving his prize from Dr. Michael Berger of Simmons College. A complete list of Education Night award winners can be found on page 16 of this issue. (Photo courtesy of Morton Z. Hoffman)*

Deadlines: *December 2010 Issue: October 13, 2010*
January 2011 Issue: November 15, 2010

THE NUCLEUS

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Book Review

Continued from page 2

metallic complexes, surfaces and the solid state are also covered. The impact of computational chemistry on the field of gold chemistry is enormous. The authors indicate that tremendous progress has been made in this discipline, but there are significant challenges that still remain. As the field of theoretical chemistry of gold develops, the impact will be seen in all disciplines of chemistry.

Chapter five focuses on the luminescence and photophysics of gold complexes. Chi-Ming Che and Siu-Weu Lai discuss the spectroscopic properties of mono-, di-, and polynuclear gold(I) and gold(III) complexes. The authors provide a detailed discussion of the electronic properties of gold complexes and their contribution to the luminescent characteristics of these complexes. In addition, a discussion of how solvent, counterions, and protonation among many other environmental influences which impact the luminescent properties of gold complexes is presented.

In chapter six, Michael W. Whitehouse and co-workers describe the preparation of gold complexes that are medicinally relevant. According to the authors, there has been increased interest in gold-based pharmaceuticals in the last few decades. Research into the biochemistry of gold was not heavily pursued until the 1970s, when research was expanded to investigate the use of gold complexes to treat rheumatoid arthritis, HIV, and cancer. This chapter opens with a general discussion of gold chemistry, including the structures of gold complexes, redox chemistry, and mechanisms of ligand exchange. A very detailed section about the preparation of biologically relevant gold complexes ensues. A section is devoted to how gold interacts with proteins, in particular the serum albumin, metallothioneins, glutathione-peroxidase, insulin, ribonuclease, zinc finger proteins, hemoglobin, and mitochondrial thioredoxin reductase. The physiological and cellular biochemistry of gold complexes is also

included. Gold(I)-based drugs are usually rapidly metabolized and are more than likely prodrugs in the human body. The authors provide a detailed account of what happens to gold complexes under physiological conditions. The future of oncology treatment may lie in gold complexes as therapeutic agents as several gold(I) and gold(III) complexes show cytotoxicity in many *cis*-platin resistant cell lines.

Chapter seven, written by M. B. Cortie and A. McDonagh, covers the nanoscience of gold and gold surfaces. An overview of the field, highlighting the chemical and physical aspects of the newest research in the field, as opposed to specific technological applications is presented. Gold is ideal to work with in nanotechnology because of its chemical stability, optical properties, and its ability to conduct heat and electricity in addition to being soft and ductile. The unique affinity of gold for sulfur has also made it an ideal material for nanotechnology. Many gold nanoparticles have biological applications, including: fluorescent biological labels, the ability to detect pathogens or proteins, blood immunoassays, and DNA analyses. Colloidal gold particles can be used to target and destroy cancer cells, macrophages, and pathogens. According to the authors, "gold is immune to the corrosion of physical environments and can safely be used to target a certain area of the body at which an action is triggered." This chapter highlights several forms of gold at the nanoscale, including: clusters, nanoparticles less than 5 nm in diameter, nanospheres, nanoshells, nanorods, mesoporous sponges, thin films, and the agglomeration of nanoparticles into disordered aggregates and colloidal crystals. The application of gold films and nanoparticles in surface plasmon resonance spectroscopy, fluorescence, luminescence and heterogeneous catalysis is also covered. A detailed discussion of the surface chemistry of gold focusing on surface bonding to atoms in addition to sulfur is included.

The final chapter of the book, written by Silverio Coco and Pablo Espinet, focuses on liquid crystals based on gold compounds. The chap-

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ter opens with a detailed explanation of the basic concepts of liquid crystals. The authors cover liquid crystals with gold complexes bearing pyridine, dithiobenzoate, isocyanide, isocyanide-halide, isocyanide-alkynyl, isocyanide-fluorophenyl, and ionic bis(isocyanide) ligands. A brief discussion of gold-based liquid crystals with pyrazole ligands, which are important in forming non-rod like shaped liquid crystals, is also included. The authors conclude the chapter with a short discussion on using gold nanoparticles in liquid crystals.

This book provides a nice overview on the applications of gold complexes in medicinal chemistry and materials science, in particular with the luminescent characteristics associated with polynuclear gold complexes. However, the explosion of gold catalysis that occurred in organic chemistry over the last few decades was not covered. Mohr indicated this was due to a

continued on page 17

Monthly Meeting

The 90th Meeting of the Northeastern Section of the American Chemical Society

Joint Meeting: Northeastern Section, ACS and the Medicinal Chemistry Group



Symposium

Emerging Treatments for CNS Disorders

Organized by the Medicinal Chemistry Group of the Northeastern Section, American Chemical Society

Thursday – September 9, 2010

Holiday Inn Hotel

15 Middlesex Canal Park Road, Woburn, MA

3:00 pm Refreshments

3:15 pm Welcome

Raj (SB) Rajur, Program Chair, CreaGen Biosciences, Inc., Woburn, MA

3:20 pm Introductory Remarks

Norton P. Peet, Director of Chemistry, Microbiotix, Worcester, MA

3:30 pm **Presentations: Confirmed speakers:**

- 1) Dr. James Rusche, Sr. VP Research and Development, RepliGen Corp., Waltham, MA
- 2) Dr. Vincent Jacques, Sr. Director, Preclinical Development, RepliGen Corp., Waltham, MA.
- 3) Dr. Larry Hardy, Director of Pharmacology, Sepracor Corp., Marlborough, MA
- 4) Dr. Ian Bell, Merck & Co. Rahway, NJ
- 5) Dr. Edward Holson, Director of Chemistry, Broad Institute, Cambridge, MA

5:45 pm Social Hour

6:30 pm Dinner

7:45 pm **Keynote Presentation**

Dinner reservations should be made **no later than 12:00 noon on Thursday, September 2nd, 2010**. Please contact Anna Singer at (phone/fax 781-272-1966) or secretary@nesacs.org. Reservations not canceled at least 24 hours in advance must be paid. Anyone who needs handicapped services/transportation, please call a few days in advance so that suitable arrangements can be made. Reservations not canceled at least 24 hours in advance must be paid. **Payment is made at the door by cash or check (no credit cards.) Members, \$28.00; Non-members, \$30.00; Retirees, \$18.00; Students, \$10.00.**

Directions to Holiday Inn Hotel

A. From Boston - Cambridge - Points North: Take Route I-93 to Route 95/128 West. After 1 mile, take Exit 35 South to Route 38 (Main Street).

After about 500 feet at the traffic light, turn right into Middlesex Canal Street to the hotel entrance.

B. From the West: Take Route 95/128 North to Exit 35 South (Route 38 - Main Street). **Follow directions listed above**

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Call For Applications

YCC/NESACS–JCF/GDCh
Exchange to Germany
March 20–27, 2011

The Younger Chemists Committee (YCC) of the Northeastern Section and the NESACS Education Committee invite applications from undergraduate and graduate students of chemistry, biochemistry, and chemical engineering at colleges and universities within the Section to spend a week in Germany as the guests of the *Jungchemikerforum* (Young Chemists Committee; JCF) of the *Gesellschaft Deutscher Chemiker* (German Chemical Society; GDCh). The group on this trip, the eleventh of the Exchange and seventh to Germany, will consist of up to 12 students and a number of faculty and industrial representatives.

The trip to Germany will begin with an overnight flight from Boston on Saturday, March 19; return to Boston will be on Sunday, March 27. The visit will include excursions to industrial, academic, scientific, and cultural institutions in the Nürnberg area, and will feature the JCF student chemistry research conference (*Frühjahrssymposium*) at the University of Erlangen-Nürnberg on Wednesday-Saturday, March 23-26, which will provide the opportunity for the participants to engage in extensive networking with German and other European students, and to take part in discussions focused on careers, education, and international opportunities. Each student representative from NESACS will be expected to make a poster or oral presentation on his/her research at the *Frühjahrssymposium*, and upon return at the Northeast Student Chemistry Research Conference (NSCRC) in April. Air tickets will be provided by NESACS; accommodations in Germany will be covered by GDCh. A working knowledge of German, while useful, will not be specifically required; the language of the *Frühjahrssymposium* and the other

Save the date!

9th Annual Undergraduate Symposium on Sustainability and the Environment

*Saturday, November 20, 2010
Bridgewater State College*

Undergraduate research posters (including completed, in progress, and proposed research) in all environmental disciplines are welcome. We are also happy to invite student presentations pertaining to campus sustainability projects, or regional/global sustainability issues.

Please email Ed Brush (ebrush@bridgew.edu) to add your name to our distribution list. A formal “Call for Abstracts” will be sent electronically in September. ◇

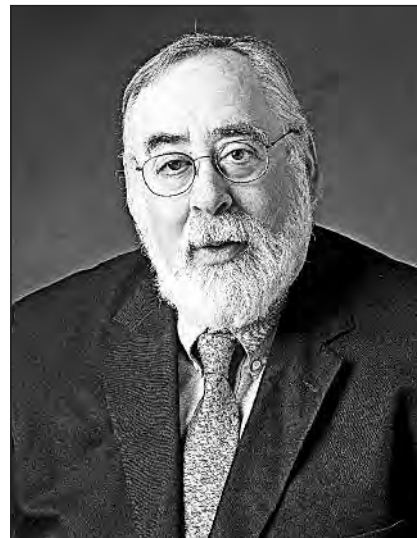
events will be English.

Application forms are available on the YCC <<http://www.nsycc.org>> and NESACS <<http://www.nesacs.org>> websites. The following material must be submitted electronically with the application form: 1) the abstract of the presentation to be made at the *Frühjahrssymposium* and the NSCRC; 2) an essay on the relevance of the exchange to the student’s professional goals; 3) a letter of recommendation from the student’s research supervisor; 4) approval from the supervisor and the chair of the department of the student’s absence from classes, the research laboratory, and other responsibilities. In addition, finalists will be interviewed by members of the Organizing Committee.

For more information, contact Dr. Michael Strem, Chair of the Organizing Committee, at <mstrem@strem.com>.

Deadline for electronic receipt of applications: November 5, 2010, at 5:00 p.m. ◇

Norris Award to Professor George Bodner



The Northeastern Section of the American Chemical Society is pleased to announce that Professor George Bodner is the winner of the 2010 James Flack Norris Award for Outstanding Achievement in the Teaching of Chemistry. Professor Bodner is the Arthur E. Kelly Distinguished Professor of Chemistry and Education at Purdue University. He previously received both the Chemical Manufacturers Association Catalyst Award in Chemical Education and the American Chemical Society Pimentel Award in Chemical Education, among many other awards. Professor Bodner played a catalytic role for incorporation of constructivist methods into chemical education and created the graduate program in chemical education at Purdue University. The Award will be formally presented to Professor Bodner at the November 11 meeting of the Northeastern Section. ◇

Your one-stop source to career-related links in the Chemical Sciences

WWW.NESACS.ORG/CAREERS

September Historical Events In Chemistry

by Leopold May, The Catholic University of America, Washington, DC

September 1, 1873

B. Smith Hopkins, who was a researcher on rare earths, was born on this date.

September 3-5, 1860

One hundred and fifty years ago during these dates, the Karlsruhe Congress, the first international meeting of chemists was held in Karlsruhe, Germany.

September 6, 1870

Frederick G. Donnan, a researcher in the theory of membrane equilibria (Donnan Equilibrium), was born on this date. He also did research in chemical kinetics.

September 9, 1858

One hundred and twenty-five years ago in 1885, Carl Auer von Welsbach, discovered neodymium (Nd, 60) and praseodymium (Pr, 59). He was a researcher on rare earths, who discovered lutetium with Georges Urbain (Lu, 71) in 1907, and invented an incandescent mantle (Welsbach Mantle or Auerlicht). He was born on this date.

September 12, 1897

Seventy-five years ago in 1835, Irène Joliot-Curie and her husband, Frédéric Joliot-Curie, were awarded the Nobel Prize in Chemistry in recognition of their synthesis of new radioactive elements. She was born on this date.

September 13, 1886

Robert Robinson, a researcher in plant pigments, alkaloids and phenanthrene derivatives, was born on this date. He was awarded the Nobel Prize in Chemistry in 1947 for his investigations on plant products of biological importance, especially the alkaloids.

September 16, 1853

One hundred years ago in 1910, Albrecht Kossel, a researcher in the chemistry of cells and proteins, was awarded the Nobel Prize in Physi-

ology or Medicine in recognition of the contributions to our knowledge of cell chemistry made through his work on proteins, including the nucleic substances. He was born on this date.

September 17, 1677

Stephen Hales studied the role of air and water in the maintenance of both plant and animal life, developed the pneumatic trough, and discovered that 'air' is released in decomposition of plant and animal substances. He was born on this date.

September 23, 1915

John Sheehan, who synthesized penicillin-V in 1957, was born on this day

September 24, 1898

Howard Walter Florey, who was born on this date, did research on lysozymes and antibiotics. In 1945, he shared the Nobel Prize in Physi-

ology or Medicine with Alexander Fleming and Ernst B. Chain for the discovery of penicillin and its curative effect on various infectious diseases.

September 26, 1754

Joseph-Louis Proust articulated the Law of Definite Proportions and was born on this date.

September 29, 1920

Peter D. Mitchell, researcher on chemiosmotic reactions and reaction systems, was born on this date. In 1978, he received the Nobel Prize in Chemistry for chemiosmotic theory and its contribution to the understanding of biological energy transfer.

Additional historical events can be found at Dr. May's website, at <http://faculty.cua.edu/may/ChemistryCalendar.htm>. ◇



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Call for Nominations

The Gustavus John Esselen Award for Chemistry in the Public Interest

The Northeastern Section (NESACS) is inviting nominations for its prestigious Gustavus John Esselen Award for Chemistry in the Public Interest. This award is given annually to a chemical scientist, whose scientific and technical work has contributed to the public well-being and has thereby communicated the positive values of the chemical profession. The significance of this work should have become apparent within the five years preceding nomination. The awardee shall be a living resident of the United States or Canada at the time of the nomination.

There is no limitation to the field of chemistry. This award differs from other ACS awards because the selection committee focuses on the general public recognition of the work but also considers its scientific/technical significance.

The Award consists of a bronze medal and the sum of \$5,000. Travel expenses incidental to the conferring of the award will be reimbursed. The award will be presented at the April 2011 meeting of the Section. The Awardee is expected to deliver an address related to the work for which the honor is conferred, but it should be oriented toward why it is in the public interest and for an audience with limited knowledge of the specific field.

Nominations should be submitted as a single pdf file including: 1) a letter signed by the primary sponsor with a description of how the nominee's work has been recognized as making a major contribution to the public welfare and as communicating positive values of the chemical profession, plus the names of two co-sponsors; 2) short supporting co-sponsor statements; 3) the nominee's professional biography including a list of no more than ten of the nominee's publications selected for their pertinence to the work nominated

Moiety

A short essay by Marshall E. Deutsch

Louis W. Mead and I, in U.S. Patents 4094647 (June 13, 1978), 4235601 (November 25, 1980) and 4361537 (November 30, 1982) described a test method which came to be called (not by us) "lateral-flow immunochemistry," and was so well adapted to simplified tests such as home pregnancy tests that our patents were cited by literally hundreds of subsequent U.S. patents.

Sometimes the holder of one of these subsequent patents would sue the holder of another of these patents for infringement, whereupon the latter would claim that he or she was not infringing on the former's patent because the former's patent was not really valid; the claims in question had really been anticipated by our prior patents, which had expired. That's where I came in. The company being sued would call me as a witness to explain how our patent had really anticipated the patent of the company which was bringing suit for infringement.

I was quite sincere in defending the breadth of our invention: in writing it I had been careful to generalize its utility by using such language as "such label may be any chemical substance or moiety having a detectable characteristic which is ...". "Moiety," I believed, meant "entity." Then, at one

for recognition; and 4) copies of popular and technical press news or feature articles indicative of public benefit and interest. Further information is available at www.nesacs.org.

Nominations Are Due October 15, 2010 to obermayer@alum.mit.edu with cc to piper281@verizon.net. Award recipients will be notified by February 1, 2011.

Inquiries may be directed to the above or to Dr. Arthur Obermayer, Tel. (617)244-0180 or Karen Piper, Tel. (978) 456-8622. Address: 19 Mill Rd., Harvard, MA 01451. ◇

of these trials, the judge asked me to define "moiety" and I hedged, suggesting that a dictionary be consulted.

I went home and looked up "moiety" in the third edition of The American Heritage Dictionary and was shocked to note that it was defined only as "1. A half. 2. A part, portion or share. 3. Either of two basic units in cultural anthropology that make up a tribe on the basis of a unilateral descent." This seemed reasonable; obviously the word is a cognate of the French "moitié."

But it seemed to me that chemists habitually used the word "moiety" to mean "entity," so I searched Google patents for the word "moiety" and found thousands of references to the word in chemical patents, and every one I checked used it the way I had used it and not with the dictionary meaning.

Then I checked other dictionaries, including the revered Oxford English Dictionary. None of them defined "moiety" as entity. They all had definitions concordant with that in the American Heritage Dictionary. And since so many chemists (who, I am sure, out-number lexicographers) use the word to mean "entity," I believe that it is lexicographers who are at fault in not listing a moiety of the meanings of moiety. Nevertheless, very large numbers of patents (I know) and scientific publications (I guess) contain a word whose meaning can be deciphered only by familiarity with its usage and not by consulting a dictionary. ◇

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National Chemistry Week Events

Celebrating



American Chemical Society
Local Section

Behind the Scenes with Chemistry October 17 - 23, 2010

October 17, 2010 – Museum of Science Boston

• *Phyllis A. Brauner Memorial Lecture by Dr. Bassam Shakhashiri*

Dr. Bassam Shakhashiri is a Professor of Chemistry at the University of Wisconsin-Madison and is the William T. Evjue Distinguished Chair for the Wisconsin Idea. Professor Shakhashiri has captivated audiences with his scientific demonstrations at a variety of locations including Boston's Museum of Science, the National Academy of Sciences and the Smithsonian's National Air and Space Museum in Washington.

Taking place in Cahners Theatre (2nd floor, Blue Wing) at 1:00 pm and 4:00 pm.

* Admission to the museum is required. Free tickets to Dr. Shakhashiri's show will be available on a first come, first serve basis. Tickets are available via advance reservation. To reserve tickets, please contact the NESACS secretary either via email secretary@nesacs.org (preferred) or by phone 1-781-272-1966 before October 14, 2010. Tickets will be available for pick-up in the lobby of the museum at the ACS table.

Kicking off National Chemistry Week 2010 festivities

Join us in a variety of hands-on activities related to the yearly theme.

Taking place from 1:00 pm - 5:00 pm on October 17, 2010 throughout the Museum.

October 23, 2010 – Boston Children's Museum

From 11 am – 4 pm, NCW volunteers will be on-hand throughout the museum to perform demonstrations and assist in hands-on activities related to the yearly theme.

September 1 – October 10, 2010

K-12 students participate in the **NCW poster competition**.

Visit www.nesacs.org and

http://portal.acs.org/portal/acs/corg/content?_nfpb=true&_pageLabel=PP_TRANSITIONMAIN&n ode_id=1033&use_sec=false&sec_url_var=region1&__uuid=9f5daa85-50f8-4707-b39b-e2ad814f3021 for more information.

October 1 – 31, 2010

Grades K-12 may participate in the **puzzle contest**.

See www.nesacs.org or the October 2010 issue of the Nucleus for the puzzles and contest information.

Summer Scholar Report

Nucleophilic Displacement Reactions in Hindered Allylic Systems

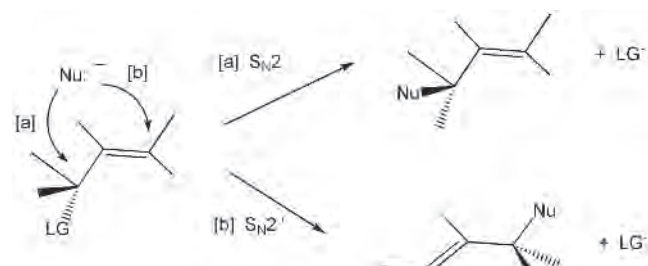
John J. Sirois

Advisor: Dr. Donald Boerth

Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth

Introduction

The S_N1 and S_N2 mechanisms are very well-known, understood pathways for nucleophilic displacement. However, allylic nucleophilic displacement reactions, otherwise known as the bimolecular substitution S_N2' pathway (Scheme 1), is less common but has attracted considerable interest.



SCHEME 1. S_N2 vs S_N2' modes of nucleophilic displacement.

Over the past sixty years a substantial amount of work has been carried out on S_N2' reactions (1-8). The concept that nucleophilic attack at the C=C bond of an allylic halide could result in a shifting of the position of the double bond with simultaneous ejection of the leaving group leading to a rearranged product has been disputed (4-6). In 1949, Kepner, Winstein, and Young (7) established a set of criteria for the S_N2' mechanism. They believed that the S_N2' designation should only be applied when second order kinetics could be established, and when it could be shown that the abnormal product did not arise from rearrangement of the starting material, or of an initially formed “normal” product. Young and his group studied the reactions of allyl halides, and their α - and γ -substituted derivatives (8). They found that most nucleophiles prefer the S_N2 pathway in allylic systems. But the reactions will prefer the S_N2' pathway when the α -methyl group was replaced by an α -chlorine or α -*t*-butyl group. The S_N2' pathway dominated when tertiary alkyl halides were used instead of secondary alkyl halides. The rate of this reaction was about twice that of the S_N2 pathway. This suggested that α -methyl substitution accelerated the S_N2' pathway. The stereochemical relationship between the entering nucleophile and the leaving group (syn vs. anti) has also been investigated (9-11).

For some time, Boerth and coworkers have studied reactions in rigid bicyclic systems (12-13). The bicyclo[4.2.1]non-3-en-2-yl system was selected to specifically study this stereochemically sensitive mechanism. The rigid nature of this ring system allows the control of the reaction pathway. Boerth and Van Catledge developed a new syn-

thetic pathway into this ring system (12). Synthesis of the bicyclo[4.2.1]non-3-en-2-one **4** was achieved by methods outlined in Scheme 2. Earlier force-field calculations, NMR, and ultraviolet spectral results clearly indicate that this ketone exists in a flattened boat conformation with good extended π conjugation (12). Ab initio SCF calculations of the geometry of this molecule at the 6-31G* level confirms these structural features (Fig. 1). In addition, the structure of the unsaturated ketone system reveals that the carbon-carbon double bond is sterically unhindered and therefore very exposed to attack. The chemistry of this system is consistent with this interpretation. The olefinic portion of this α,β -unsaturated ketone, for example, is very susceptible to reaction as evidenced by the facile formation of epoxide and cyclopropane derivatives, as well as 1,4-Michael addition with 1,4-butanedithiol.

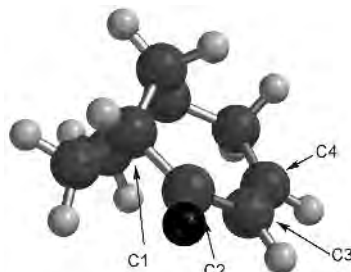
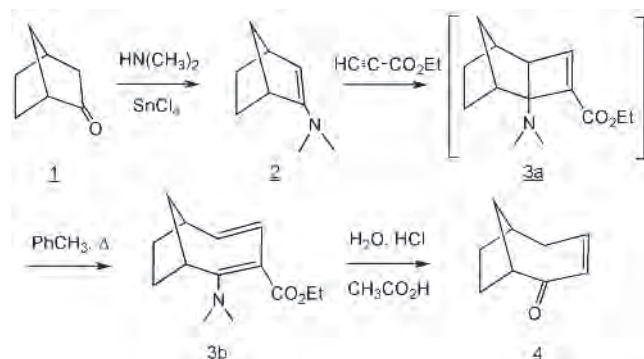


FIGURE 1. Bicyclo[4.2.1]non-3-en-2-one geometry optimized at RHF-6-31G

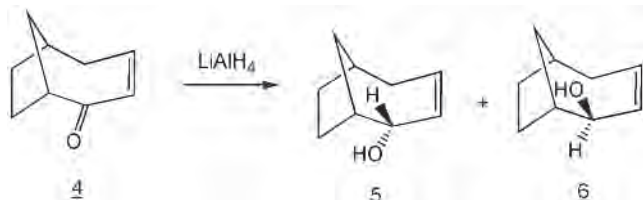


SCHEME 2. Preparation of Bicyclo[4.2.1]non-3-en-2-one (4).

Despite the reactivity of the carbon-carbon double bond, reaction does take place, nonetheless, at the carbonyl. Reduction with lithium aluminum hydride is particularly facile and clean, yielding exclusively the endo-bicyclo[4.2.1]non-3-en-2-ol **5** in 95% yield (Scheme 3). Production of the endo-alcohol is reasonable since, as in

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SCHEME 3. Lithium aluminum hydride reduction of **4**

2-bicyclo[2.2.1]heptanone reductions, the carbonyl is much more accessible from the exo face of the molecule (14).

Attempts at further reduction of the carbonyl revealed some interesting aspects of the mechanism of the allylic nucleophilic substitution. The rigid bicyclo[4.2.1]non-3-en-2-yl system was a convenient structure on which to explore the relationship of stereochemistry and regiochemistry required for the S_N2' nucleophilic displacement in hindered allylic systems.

Results and Discussion

Our study focused on the quantitative determination of the preference of the S_N2' over S_N2 reactions of substrates with sterically hindered and stereochemically unique leaving groups. Entry into this system was obtained by the reduction of bicyclo[4.2.1]non-3-en-2-one with $LiAlH_4$ to yield bicyclo[4.2.1]non-3-en-2-ol **5** (Scheme 3). The stereochemistry of the alcohol was established to be exclusively the endo-isomer. Sadlo and Kraus (15) synthesized both the exo- and endo-alcohol isomers from 3,3-dihalotricyclo[4.2.1.0]nonyl derivatives. They reported chemical shifts for the methine proton at 4.25 ppm in the endo-alcohol and at 3.98 ppm in the exo-alcohol. Our NMR spectrum of the alcohol contained a distinct methine proton at 4.27 ppm and no methine proton was present at 3.98 ppm (Fig. 2).

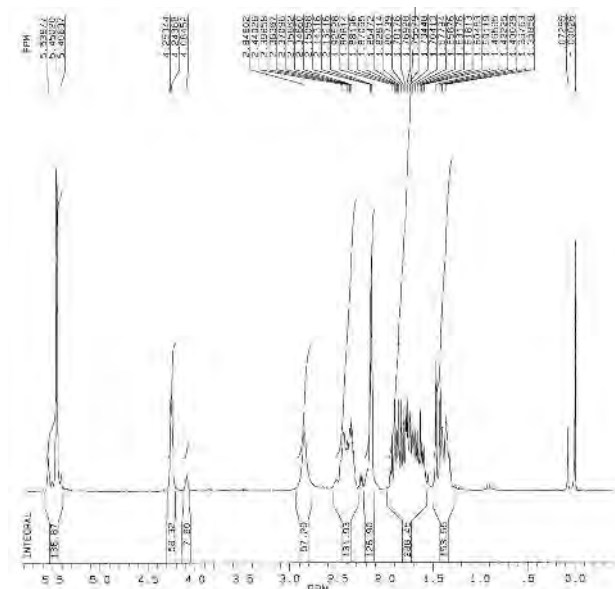
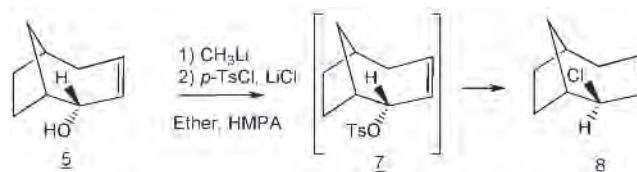


Figure 2. 1H NMR of bicyclo[4.2.1]non-3-en-2-ol **5**

Suitable leaving groups were introduced from the endo-alcohol **5**. Endo-bicyclo[4.2.1]non-3-en-2-yl *p*-toluenesulfonate **7** and exo-2-chlorobicyclo[4.2.1]non-3-ene **8** were synthesized using the methods in Scheme 4. These compounds were prepared by a modified method of Stork (16) by treating the alcohol **5** with methyl lithium followed by *p*-toluenesulfonyl chloride. In an ether-HMPA solution, we obtained exo-allylic chloride **8** with only a small amount of endo-tosylate **7**. (Figure 3 displays the proton NMR spectrum of **8** following silica gel chromatography.) Initial deprotonation of the alcohol by methyl lithium leads to the corresponding alkoxide which attacks the *p*-TsCl to give only the endo-tosylate because the stereochemistry is not altered by the methyl lithium attack or the tosylation reaction. Recovery of the tosylate from the reaction mixture was not possible because of the susceptibility of the tosylate to attack by the released chloride ion. Displacement of the tosylate by nucleophilic substitution by the chloride ion from the backside (S_N2) with inversion produces the exo-chloro compound **8** as the only product. The dipolar aprotic nature of the HMPA solvent results in poor solvation of the chloride ion. This leaves the chloride ion readily available to displace the tosylate group from backside attack. Added lithium chloride insures clean conversion to the exo-2-chloro derivative.



SCHEME 4. Preparation of exo-allylic chloride **8**

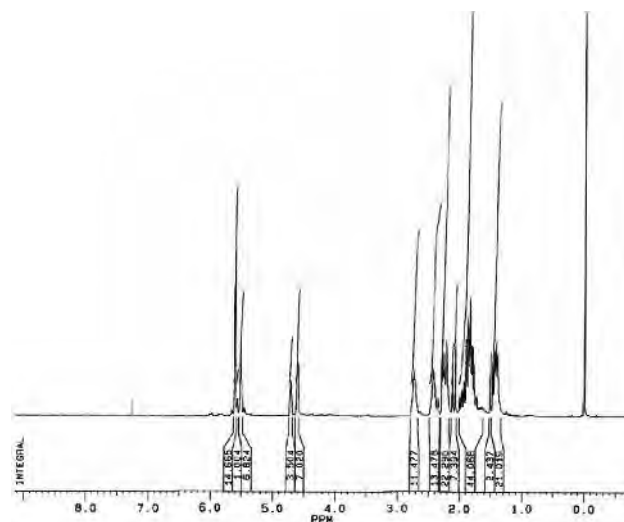


Figure 3. 1H NMR spectrum of Exo-2-chlorobicyclo[4.2.1]non-3-ene

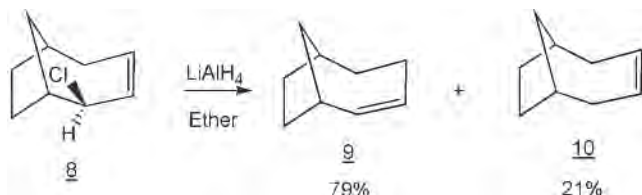
Nucleophilic displacement was carried out on exo-2-chlorobicyclo[4.2.1]non-3-ene **8** using hydride as the nucleophile shown in Scheme 5. Reduction with lithium

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aluminum hydride yielded a mixture of 2-bicyclo[4.2.1]nonene **9** and 3-bicyclo[4.2.1]nonene **10** by displacement of chloride.



SCHEME 5. Allylic nucleophilic reduction of **8** using hydride as the nucleophile.

This isomeric mixture was analyzed by GC-mass spectrometry (Figs. 4,5,6) and also by FT-NMR (Figs. 7,8). The NMR data for the olefinic protons allowed us to identify each isomer synthesized. The isomers are distinguishable because the olefinic protons of symmetric 3-bicyclononene appears as a broadened singlet at $\delta 5.41$ ppm with weak coupling to neighboring protons. In contrast, the olefinic protons in 2-bicyclo[4.2.1]nonene have different chemical shifts downfield from the olefinic protons in 3-bicyclononene and strong coupling with neighboring protons. Integration of the two regions gives the product distribution for the two isomers. Combining this with the total ion chromatogram from GC-MS analysis allowed us to identify each isomer and to determine the product ratios, from the integrated peak areas (Fig. 4). We obtained 79% of the rearranged product, 2-bicyclononene **9** and only 21 % of the unrearranged 3-bicyclononene **10**. Backside attack by the hydride via the $\text{S}_{\text{N}}2$ mechanism must take place from the sterically hindered endo face of the bicyclo[4.2.1]nonene ring. This leads to only a small percentage of the 3-isomer. In contrast, nucleophilic approach at C4 in the allylic system is unhindered. Nucleophilic attack by hydride at C4 leads to $\text{C}=\text{C}$ bond migration with loss of chloride ion. This facile $\text{S}_{\text{N}}2'$ process leads to the predominant major 2-ene product **9**.

To synthesize the endo-tosylate **7**, the tosylation reaction was carried out in THF instead of HMPA according to Scheme 6. After treatment of the endo-alcohol **5** with methyl lithium and *p*-TsCl in THF, again attempts to isolate the endo-tosylate were unsuccessful. However, after generation of the tosylate in situ, without further nucleophilic substitution by chloride, reduction by lithium aluminum hydride gave the opposite alkene product distribution from that obtained by reduction of the exo-chloro compound **8**. GC-MS analysis (Fig. 9) and proton NMR (Figs. 10,11) show that only 41% of the 2-bicyclononene **9** and 59% 3-bicyclononene **10** was present (Figs. 9,10,11). Apparently, hydride attack took place from the exo-face of the molecule by $\text{S}_{\text{N}}2$ displacement of tosylate from the endo side of the molecule. Under these conditions, the $\text{S}_{\text{N}}2$ mechanism dominated, while the primary pathway for the chloro compound **8** was $\text{S}_{\text{N}}2'$ because the endo-face was hindered.

We expected the yield of 3-bicyclononene to increase

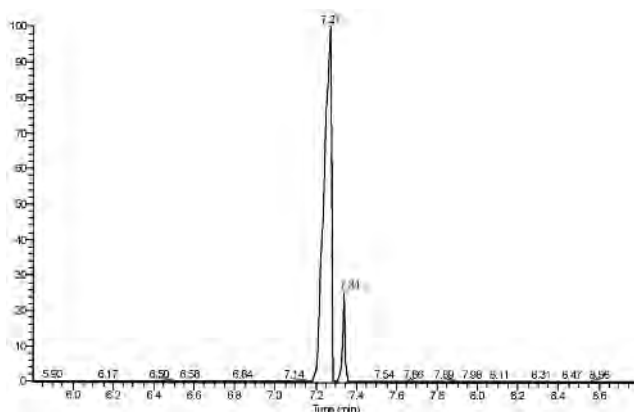


Figure 4. Total Ion Chromatogram of Bicyclo[4.2.1]nonene Mixture from Ether-HMPA [Retention Times: 7.27 min (2-bicyclononene) 7.34 min (3-bicyclononene)]

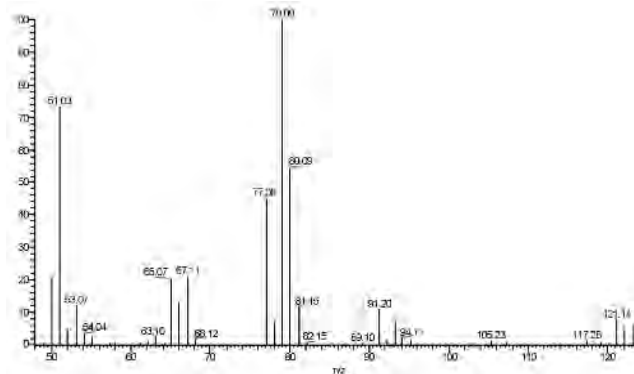


Figure 5. Mass Spectrum of 2-Bicyclo[4.2.1]nonene

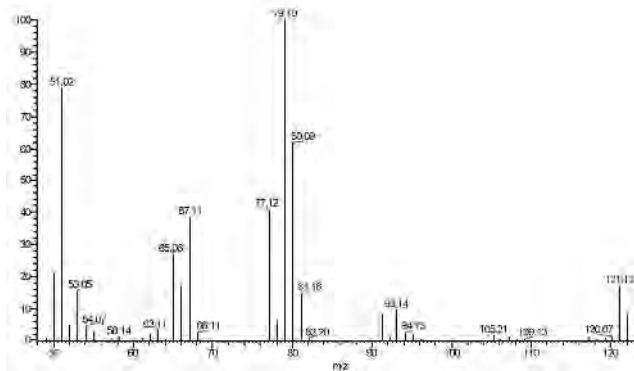


Figure 6. Mass Spectrum of 3-Bicyclo[4.2.1]nonene

because the initial reaction was expected to stop at the unhindered tosylate which would be easily reduced preferentially to **10**. Conversely, when tosylation of the endo-alcohol was carried out in an apolar solvent (HMPA), exo-2-chlorobicyclo[4.2.1]non-3-ene was isolated. Subsequent LiAlH_4 reduction of this exo-2-chloride led almost exclusively to the rearranged 2-bicyclononene product **9** from an $\text{S}_{\text{N}}2'$ mechanism. The reversal of mechanism and product distributions from exo vs. endo leaving groups is consistent with the relative accessibility to the backside of the reaction center imposed by the steric and stereochemical

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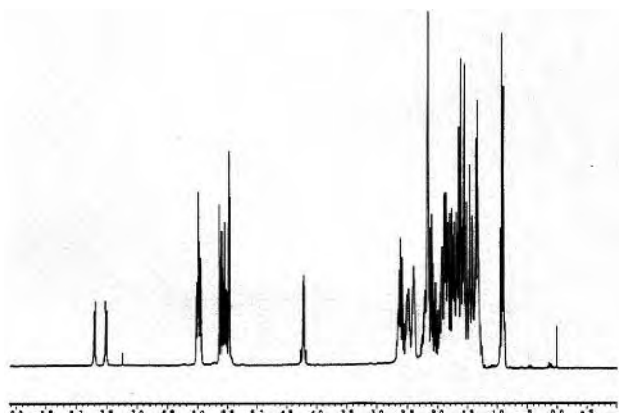


Figure 7. ^1H NMR of Bicyclo[4.2.1]nonene Mixture **9** & **10** from LiAlH_4 with *Exo*-2-chlorobicyclo[4.2.1]non-3-ene

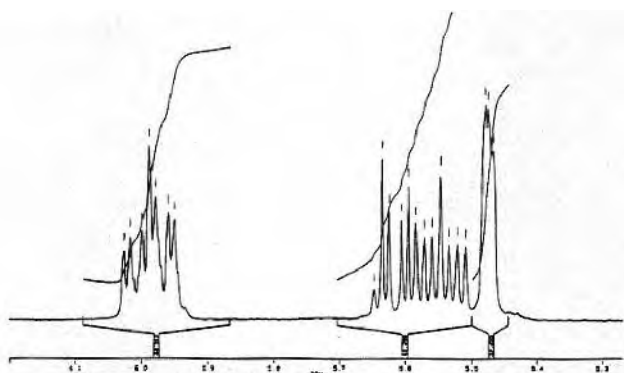
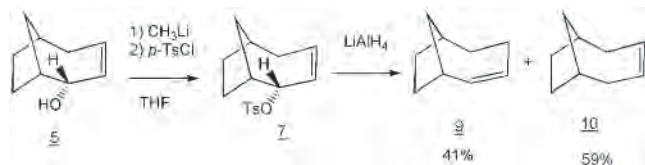


Figure 8. Olefinic Portion of ^1H NMR of Alkene Mixture **9** & **10** from LiAlH_4 with *Exo*-2-chlorobicyclo[4.2.1]non-3-ene (Region 5.2-6.2 ppm expanded)



SCHEME 6. Allylic nucleophilic reduction of **Z** using hydride as the nucleophile.

constraints of the ring system. The ratio of the percent composition of 2-bicyclononene to 3-bicyclononene is a direct measurement of the ratio of $\text{S}_{\text{N}}2'$ to $\text{S}_{\text{N}}2$ pathways.

Conclusions

It can be concluded that allylic compounds undergo displacement reactions in direct relation to the relative accessibility or inaccessibility of the back side of the leaving group. Allylic systems with unhindered back sides tend to undergo normal $\text{S}_{\text{N}}2$ displacement. The $\text{S}_{\text{N}}2'$ mechanism pathway will occur when the backside of the system is highly hindered. Solvent effects can also contribute to these mechanistic pathways by reactivity and solvation of the nucleophile. This mechanism will only dominate over the normal $\text{S}_{\text{N}}2$

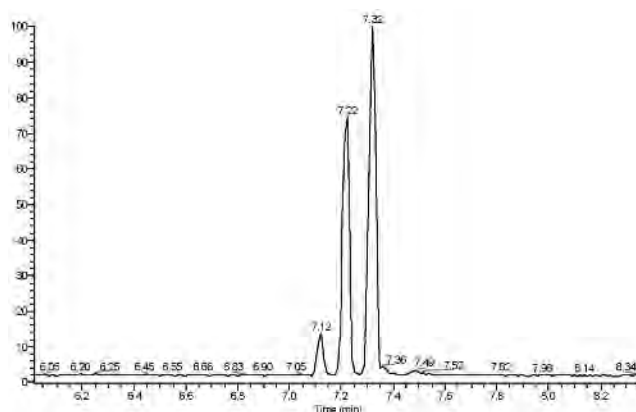


Figure 9. Total Ion Chromatogram of Bicyclo[4.2.1]nonene Mixture in THF [Retention Times: 7.22 min (2-bicyclononene), 7.32 min]

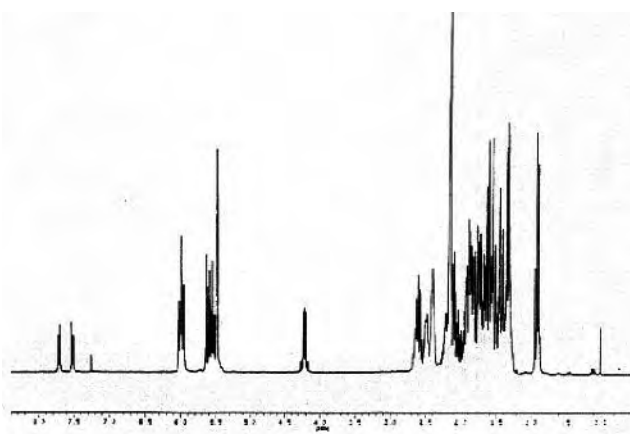


Figure 10. ^1H NMR of Alkene Mixture **9** & **10** from LiAlH_4 and *Endo*-bicyclo[4.2.1]non-3-en-2-yl *p*-toluenesulfonate Formed In Situ in Ether-THF

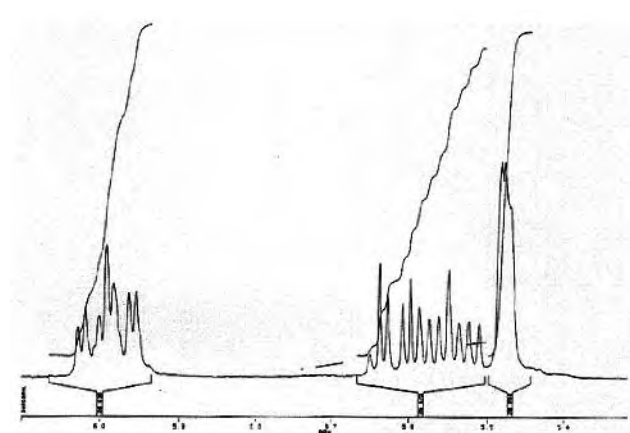


Figure 11. Olefinic Portion of ^1H NMR of **9** & **10** from LiAlH_4 and *Endo*-bicyclo[4.2.1]non-3-en-2-yl *p*-toluenesulfonate Formed In Situ in Ether-THF (Region 5.2-6.2 ppm Expanded)

pathway when favored by steric, conformational or polar interactions.

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Experimental Section

Instrumentation:

A Bruker 300 MHz FT-NMR and a Varian Associates EM-360A-60MHz NMR were used to obtain ^1H NMR spectra with chemical shifts given in ppm downfield from tetramethylsilane. A Perkin-Elmer IR-1310 instrument was used to record infrared spectra. Bands were reported in cm^{-1} . A Gow-Mac series 350 gas chromatograph with a thermal conductivity detector and a non-polar DC200 (20%) on Chromosorb-P 80/100 mesh (4' x 1/4") column and DACS Chromatography-Software were used to carry out the gas chromatographic analysis. The GC/MS analysis was obtained using a Thermo-Scientific Focus GC-ITQ 700 MS.

Preparation of 2-(N,N)-dimethylaminobicyclo[2.2.1]-hept-2-ene (2):

63.67g (0.56 mol) of 98% 2-norboranone 1 was dissolved in 1 L of dry pentane in a two liter three-neck round bottom flask under nitrogen which was fitted with a mechanical stirrer and two inlet tubes. 280g (6.21 mol) of anhydrous dimethylamine was bubbled into the flask at 0°C . 45 mL (100.24g, 0.38 mol) of stannic chloride in 40mL of pentane was introduced dropwise via a dropping funnel in two equal portions. After addition at 0°C , the reaction mixture was allowed to stir at room temperature under a positive pressure nitrogen atmosphere for approximately 72 hours. A medium porosity fritted funnel with a layer of celite was used to filter the reaction mixture. The unreacted dimethylamine and pentane were removed by distillation. The enamine product was collected by fractional distillation and the final mass was determined to be 43.28g (0.38 mol) (65.32 % yield) ^1H NMR (CDCl_3) (ppm) 0.9-2.0 (6H, m), 2.62 (3H, s), 4.42 (d of d C-3-H). [reported (12) ^1H NMR (CDCl_3) (ppm) 1.5 (C-5, C-6, C-7, H, m), 2.9 (C-1, C-4, H, m), 2.62 (2CH₃, m), 4.42 (d of d C-3 H).

Preparation of Ethyl-2-(N,N)-dimethylamino)-bicyclo[4.2.1]nona-2,4-dicarboxylate (3a):

43.28g (0.37 mol) of enamine 2 and 90mL of dry toluene was added to a 500mL three-neck round bottom flask which was fitted with a magnetic stirrer, dropping funnel, and a nitrogen inlet tube. The system was flushed with nitrogen then the gas inlet valve was replaced by a stopper and the outlet valve was replaced by a drying tube. After dropwise addition of 27.81 g (0.19 mol) of ethyl propynoate to the flask, the solution was slowly brought to a reflux. After about 18 hours of reflux the mixture was rotary evaporated to remove unreacted ethyl propynoate and toluene yielding 71.51g (0.31 mol) (85.34 % yield) of crude carboxylate. NMR Analysis of this compound agreed favorably with previously reported spectra (12)

Preparation of Bicyclo[4.2.1]non-3-en-2-one (4):

A 500mL round bottom flask was fitted with a magnetic stirrer and a condenser. 71.51g (0.31 mol) of carboxylate 3b

and 100mL of glacial acetic acid were introduced into the flask. A solution of 25 mL of distilled water and 25 mL of concentrated hydrochloric acid were then added to the mixture. The reaction was refluxed for 23 hours and then transferred into a 1L separatory funnel containing 300 mL of distilled water. The mixture was extracted three times with 200mL of diethyl ether. The ether layer was then washed with three 100 mL portions of 10% sodium hydroxide solution until basic, and finally with 50 mL of saturated sodium chloride solution. The ether layer was dried over anhydrous magnesium sulfate, and then the ether was removed from the crude ketone by rotary evaporation. The ketone product was purified by fractional distillation under vacuum using a 12" column packed with glass helices and a 6" condenser. Fractions boiling at 65°C at 1.00 mmHg yielded 11.63g (22.03 % yield) of 100% pure ketone. Purity was determined using IR and GC analysis. IR: 3020, 2940, 2870, 1700, 1650, 1470, 1465, 1415, 1400, 1370, 1340, 1220, 1125, 1070, 895, and 820 cm^{-1} . ^1H NMR 60 MHz (CDCl_3) (ppm). 6.21 (1H, d of d of d of d), 5.82 (1H, d of d of d of d), 2.98 (1H, m), 2.60 (3H, m), 1.95 (5H, m), 1.62 (1H, m). [reported (12) IR (neat) 3017, 2940, 2871, 1661, 1450, 1418, 1402, 1340, 1283, 1223, 1129, 898, 819 cm^{-1} . ^1H NMR (CDCl_3) (ppm) 1.62 (1H, m), 1.95 (5H, m), 2.6 (3H, m), 2.98 (1H, m), 5.82 (1H, d of d of d of d), 6.21 (1H, d of d of d of d)]

Preparation of Endo-bicyclo[4.2.1]non-3-en-2-ol (5):

100mL of dry ether was added into a 250 mL oven dried, three-neck round bottom flask. The flask was fitted with a condenser and a dropping funnel and the system was flushed with nitrogen. Then 3.765g (0.0286 mol) of pure ketone 4 in 25mL of dry ether at room temperature was added to the flask, followed by dropwise addition of 3.934 g (0.103mol) of LiAlH_4 . This mixture was refluxed for about 3 hours and then placed in an ice bath. 10 mL of water at 0°C was added slowly to the solution followed by 15mL of 15% (w/v) sodium hydroxide. 100 mL of ether and 20 mL of distilled water were then added successively. This mixture was stirred for about 15 minutes and was washed with 100 mL of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether was filtered off and rotary evaporated leaving 3.15 g (0.0226mol) of crude alcohol (80.0 % yield). The alcohol was purified by column chromatography using 80 grams of 60-200 mesh silica gel activated at 200°C for 24 hours. The column was eluted successively with 150mL of hexane, 150 mL of 5% ether-hexane, 150 mL of 10% ether-hexane, 150 mL of 30% ether-hexane, 100 mL of 40% ether-hexane, and 100 mL of 100% ether. Fractions were collected in 20 mL portions and the desired alcohol was eluted in the 30% ether-hexane fractions. The purity of each fraction was verified by IR spectroscopy. IR: 3500-3050 (broad), 2990, 2945, 2870, 1660, 1445, 1425, 1080, 1025, 975, 895, 805, cm^{-1} . ^1H NMR 300 MHz- (CDCl_3) (ppm) 5.45 (2H, s), 4.25(1H, s), 2.85 (-OH, s), 2.40 (1H, m), 2.35 (1H, m), 2.14 (2H, s), 1.85 (2H, m), 1.68 (2H, m), 1.44 (1H, d), 1.36 (1H, t).

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Preparation of exo-2-chloro-bicyclo[4.2.1]non-3-ene (8):

A 100 mL three-necked round bottom flask was fitted with a condenser and flushed with nitrogen gas. 2.007 (0.0144mol) of alcohol 5 and 14 mL of dry 2:1 ether:HMPA solution were added to the flask which was cooled to 0 °C. 9.4 mL (0.0147mol) of 1.56 M MeLi solution was added by syringe through a rubber septum over a period of 5 min. Then 2.813g (0.0148mol) of p-TsCl in 14 mL ether:HMPA solution was added dropwise. 0.624 g (0.1473mol) of anhydrous LiCl was added to the solution, and the ice bath was removed. After 24 hours 67mL of ether and 25mL of ice cold distilled water was added and the solution was transferred to a 250mL separatory funnel. The reaction mixture was washed with two portions of 23mL of ice cold distilled water and finally with 54mL of a saturated NaCl solution. The ether layer was dried over anhydrous MgSO₄ for 30 min and rotary evaporated at 40°C to yield 2.075g (0.0132mol) of crude product. This was purified by column chromatography using 20 grams of 60-200 mesh silica gel activated at 200 °C for 24 hours. The column was eluted successively with 150mL of hexane, 50 mL of 5% ether-hexane, 50 mL of 10% ether-hexane, 50 mL of 40% ether-hexane, and 50 mL of 100% ether. The desired product was collected in the 10% ether-hexane fraction to yield 0.771g (0.0049mol) (34.12 % yield) of pure product. (¹H NMR 300 MHz) (CDCl₃) (ppm) 5.61 (2H, s), 5.49 (2H, s), 4.6-4.7 (1H, m), 4.8-5.0 (1H, s).

Preparation of the Bicyclo[4.2.1]nonene mixture (9, 10) from exo-chloro compound (8) in Ether:

A 50 mL three-necked round bottom flask was fitted with a condenser and flushed with nitrogen gas. 0.258g (0.00688mol) of LiAlH₄ in 7 mL of dry ether was added to the flask which was cooled to 0°C. 0.771g (0.00164 mol) of the purified exo-chloro compound 8 in 11.4 mL anhydrous ether was added dropwise over a period of 5 minutes. After the addition was complete the reaction mixture was stirred for 20 hours at 63° C. The reaction mixture was allowed to reach room temperature and then 3 mL of 15 % NaOH, 1.5 mL of ice cold water and 40 mL of ether were added. After filtering and washing the mixture in ether, the ether layer was washed with 30.0 mL saturated NaCl solution. The ether solution was dried over anhydrous MgSO₄ and distilled off to 10 mL using a short path distillation apparatus producing 0.605g (0.0049mol) (72.13 % yield). The crude alkene mixture was then purified by semi-preparative gas chromatography using a 20% DC710 on Chromosorb-P column (8' x 1/4", 80/100 mesh). (¹H NMR 300 MHz) – (CDCl₃) (ppm) 1.3-2.8 (12H, m, in 9 and 10), 5.47 (2H, bs, in 10), 5.5-5.65 (1H, m, in 9), 5.9-6.05 (1H, m, in 9) [reported (15) ¹H NMR (CDCl₃) (ppm) 1.2-2.8 (12H, m), 5.2-6.2 (1H, m, in 9), 5.4-6.3 (1H, m, in 9), 5.47 (2H, s, in 10)]

Preparation of the Bicyclo[4.2.1]nonene mixture (9, 10) from endo Alcohol (5) in THF:

A 100 mL three-necked

round bottom flask was fitted with a condenser and flushed with nitrogen gas. 1.605g (0.012mol) of alcohol 5 and 18 mL of dry THF were added to the flask which was cooled to 0 °C. 7.00 mL (0.0112mol) of 1.6 M MeLi solution was added by syringe through a rubber septum over a period of 5 min. The solution was stirred for 20 min. Then 2.276g (0.0120mol) of p-TsCl in 14 mL ether was added dropwise. After stirring the mixture at 0 °C for 2 hours, 1.145 g (0.030mol) of LiAlH₄ was added into the flask. After the addition was complete the reaction mixture was stirred for 28 hours at 15 °C. The reaction mixture was allowed to reach room temperature and then 3 mL of 15 % NaOH, 1.5 mL of ice cold water and 40 mL of ether were added. After filtering and washing the mixture in ether, the ether layer was washed with 30.0 mL saturated NaCl solution. The ether solution was dried over anhydrous MgSO₄ and distilled off to 10 mL using a short path distillation apparatus. The crude alkene mixture was then purified by semi-preparative gas chromatography using a 20% DC710 on Chromosorb-P column (8' x 1/4", 80/100 mesh). (¹H NMR 300 MHz) – (CDCl₃) (ppm) 1.3-2.8 (12H, m, in 9 and 10), 5.47 (2H, bs, in 10), 5.5-5.65 (1H, m, in 9), 5.9-6.05 (1H, m, in 9) [reported (15) ¹H NMR (CDCl₃) (ppm) 1.2-2.8 (12H, m), 5.2-6.2 (1H, m, in 9), 5.4-6.3 (1H, m, in 9), 5.47 (2H, s, in 10)]

Acknowledgements

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Bibliography

1. C.K. Ingold, "Structures and Mechanism in Organic Chemistry," 2nd Ed., Cornell University Press, Ithaca, **1969**, pp. 855-860.
2. P.D. de la Mare, "Molecular Rearrangements," vol. 1, P. de Mayo, ed., Interscience, New York, **1963**, p. 35.
3. R.A. Sneen, *Acc. Of Chem.*, **1**, 46, (**1973**).
4. F.G. Bordwell, *Acc. Of Chem. Res.*, **3**, 281, (**1970**) and references cited therein.
5. F.G. Bordwell and G.A. Pagani, *J. Am. Chem. Soc.*, **97**, 118, (**1975**).
6. F.G. Bordwell and T.G. Mecca, *ibid*, **97**, 123,127, (**1975**). F.G.
7. Kepner, R. D.; Winstein, S.; Young, W. G., *J. Am. Chem. Soc.*, **71**, 115, (**1949**)
8. Young, W. G.; Webb, I. D.; Goering, H. L., *J. Am. Chem. Soc.*, **73**, 1076, (**1951**)
9. Georgoulis, C. and Ville, G., *Bull. Soc. Chim. Fr.*, **3**, 485, (**1985**)
10. Murahashi, S. and Tanigawa, Y., *Kagaku (Kyoto)*, **35**, 952, (**1980**)
11. Magid, R. M. and Fruchey, O. S., *J. Am. Chem. Soc.*, **101**, 2107, (**1979**)

continued on page 17

Education Night Awards

Presented at Emmanuel College, Boston, Massachusetts, May 13, 2010

HIGH SCHOOL AWARDS

FIFTY-FIRST ANNUAL AVERY A. ASHDOWN HIGH SCHOOL EXAMINATION CONTEST

Student School Teacher

First Place - The Simmons College Award

James Lim Phillips Academy/Andover Paul Cernota

Second Place

Jin Change Middlesex School Michael Shaeberle

Third Place(Tie)

Johnathon Cai PhillipsExeter Academy Sharon Finley
Tim Caradonna Wayland High School Jay Chandler
Kyle Donahue Natick High School Kathleen Browne
Sherrie Wang Sharon High School Shawn Kenner

Honorable Mention - First Year

Ryan Budrick Wayland High School Corey Lowen
Go Keegan Lexington High School Janice Compton
Winnie Wang The Winsor School Mary Espanol
Michael Zhang Belmont High School Jean Manes

Honorable Mention – Second Year

Vyassa Baratnam Acton-Boxborough HS David Baumritter
Theresa Cloutier Andover High School Betty Iannuccioli
Ryan Heden Hollis-Brookline HS Gina Bergkaug
Daniel Hoadley Wayland High School Jay Chandler
Pratiksha Yalakkishettar Andover High School Betty Iannuccioli
Tomer Reiter Newton South HS Patrick McFarland
Sarah Shopley Hollis-Brookline HS Gina Bergkaug
Tony Wang Newton South HS Patrick McFarland
Troy Welton Woburn High School Kunjumol Joseph
Jessica Weng Phillips Academy Andover Brian Faulk

AULA LAUDIS SOCIETY

Margaret O'Connell Retired, Brockton High School
Fifty-Year Member of ACS
David Baumritter Acton-Boxborough High School
Kristen Cacciadore East Boston High School
Cricket McCaffrey-Clark Concord-Carlisle High School

Theodore William Richards Award for Excellence in Teaching Secondary School Chemistry

John Mauch Franklin High School

PROJECT SEED

Stonehill College

Mentor: Dr. Cheryl Schnitzer

Hao Trieu Randolph High School

Mentor: Dr. Louis Liotta

Joel Anifowse Brockton High School

Basem Sadaka North Quincy High School

COLLEGE AND UNIVERSITY AWARDS

2010 UNDERGRADUATE RESEARCH SCHOLARS JAMES FLACK NORRIS

AND

THEODORE WILLIAM RICHARDS SCHOLARS

College of the Holy Cross

Brian Blum Prof. Amber M. Hupp, Advisor

Characterization of Zwitterionic C18 Stationary Phases Used in Liquid Chromatography

Bridgewater State College

Melissa Brulotte Prof. Samer Lone, Advisor

The Crystal Structure of Spo4 with N-Acetyl-2-Aminofluorene

Boston University

Jiazuo Feng Prof. Mark Grinstaff, Advisor

Photo-expansive Nanoparticles: Synthesis, Characterization, and in-vitro Efficacy of a Photo-Sensitive Polymeric siRNA Delivery System.

Massachusetts Institute of Technology

Kathleen E. Fleming Prof. Joanne Stubbe, Advisor

Mechanistic Studies of Inactivation of Class Ia Ribonucleotide Reductases by Clolar

NESACS UNDERGRADUATE GRANTS-IN-AID

Emmanuel College

Vy Nguyen Prof. Ryvkin, Advisor

Effects of Tryptophan Residue Modifications on the Structure and Activity of the Copper-Containing Enzyme, Lysyl Oxidase

University of Massachusetts, Dartmouth

John Sirois Prof. Donald Boerth Advisor

Nucleophilic Displacement Reactions in Hindered Allylic System

University of New Hampshire

Thaddeus Webster Prof. Ihab Farag, Advisor

Enhancing Algae Lipid and Biodiesel Production by Temperature Stressing

Massachusetts Institute of Technology

Jin Xin Prof. Alice Ting, Advisor

Site-Specific Targeting of Small Molecules for Live-Cell and Super-Resolution Imaging

DR. PHYLLIS A. BRAUNER MEMORIAL BOOK AWARD

University of New Hampshire

Thaddeus Webster Prof. Ihab Farag, Advisor

Enhancing Algae Lipid and Biodiesel Production by Temperature Stressing

BUSINESS DIRECTORY

Book Review

Continued from page 4

subsequent book published by Wiley in 2009. It is without a doubt that the field of organic chemistry has been profoundly affected by gold catalysis and this would be a nice addition to a book which discusses the most active areas of gold research.

The organization of the book for a reader who is not familiar with all of the topics covered is disjointed. There are only two chapters which cover the application of gold complexes in medicinal chemistry, one appearing in each section. The later chapter provides a basic understanding of gold chemistry which would be useful in the former. The disjointed nature of the book is also apparent with the topic of liquid crystals. In the third chapter, gold complexes which are liquid crystals are presented without the basic concepts behind liquid crystals. For those unfamiliar with these concepts, they are presented at the beginning of chapter eight. Despite these shortcomings, this book does present an excellent discussion of the impact of gold in certain disciplines of chemistry and prepares the reader for a profound impact of gold in several applications in the future. ◇

Summer Scholar

Continued from page 15

12. D.W. Boerth and F. A. Van-Catledge, *J. Org. Chem.*, **40**, 3319 (1975).
13. F.A. Van-Catledge, D.W. Boerth, and J. Kao, *J. Org. Chem.*, **47**, 4096, (1982)
14. H.C. Brown and H.R. Deck, *J. Am. Chem. Soc.*, **97**, 5620, (1965)
15. H. Sadlo and W. Kraus, *Tetrahedron*, **34**, 1965 (1978).
16. G. Stork, P. Frieco, and M. Gregson, *Tetrahedron Lett.*, **no. 18**, 1393 (1969).
17. J. Doran, unpublished results, (2007)
18. S. M. Sazzad Hussein, M.S. Thesis, University of Massachusetts, Dartmouth, (1997) ◇

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Note also the Chemistry Department web
pages for travel directions and updates.

These include:

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www.umassd.edu/cas/chemistry/seminars.cfm

www.uml.edu/Dept/Chemistry/speakers.html

<http://www.unh.edu/chemistry/seminars.html>

Sept 14

Prof. Jin-Quan Yu (Scripps Research Institute)

“Accelerated C-H Activation Reactions:
Enantioselectivity and Positional
Selectivity”

Boston College, Merkert 130

4:00 pm

Prof. Richard Osgood (Columbia Univ.)

Tufts University Pearson Chemistry Building,
Room P-106

4:30 pm

Sept 21

Prof. Sergiy Minko (Clarkson Univ.)

“Stimuli-responsive nanostructured materials:
design and applications”

Tufts University, Pearson Chemistry Building,
Room P-106

4:30 pm

Sept 28

Prof. Reginald Penner (U.Cal., Irvine)

“Lithographically Patterned Nanowires in
Chemical Analysis”

Tufts University, Pearson Chemistry Building,
Room P-106

4:30 pm

Sept 30

Professor Gerald J. Meyer (Johns Hopkins
Univ.)

Chemistry and Sustainability Lecture Series

University of New Hampshire, Iddles,
Room L103

11:10 am

Notices for The Nucleus Calendar of Seminars should be sent to:

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Education Night

at Emmanuel College, Boston, Massachusetts, May 13, 2010

Photos Courtesy of Morton Z. Hoffman.



Margaret O'Connell (Brockton High School, retired; 50-year ACS member) (right), inductee into the Aula Laudis Society, with Bette Bridges (Bridgewater-Raynham High School), a member of the Aula Laudis Committee and Ms. O'Connell's former student.



Dave Baumritter (Acton-Boxborough High School), inductee into the Aula Laudis Society, flanked by the Co-chairs of the Aula Laudis Committee, David Olney (left) and Harvey Gendreau.



John Mauch (Franklin High School) (right), winner of the Theodore William Richards Award for Excellence in Teaching Secondary School Chemistry, with his wife, Linda Mauch (Natick High School), a past recipient of the award, and Steve Lantos (Brookline High School), Chair of the NESACS High School Education Committee, also a past recipient of the award.



—Recipients of Honorable Mention—Second Year in the Avery Ashdown High School Examination Contest: (from right) Vyassa Baratnam (Acton-Boxborough Regional High School), Daniel Hoadley (Wayland High School), Jessica Weng (Phillips Academy Andover). At the far left: Ms. Kunjumol Joseph accepts the award for her student, Troy Welton (Woburn High School). In background: Dr. Peter Nassiff (Burlington High School), Chair of the Ashdown Examination Committee.