



In Conjunction with the American Chemical Society Student Affiliates at the University of Pittsburgh



Volume 25, Issue 4

WELCOME BACK!

January 8, 2016

Happy, happy New Year and welcome back! It's 2016 and we have another long, exhilarating, arduous, super-duper, crazy fun semester ahead. With every new year comes the opportunity to look back, reflect and think about the year before. Not only to think about your accomplishments, but how did you grow? How are you a better person in 2016 than in 2015? Or maybe you're worse! In which case, stop that! What're you doing?? We don't need more jerks around!

But really, take some time and think about yourself, academically and beyond. Congratulate yourself, treat yourself, buy yourself some flowers and take yourself out for dinner. It's been a hard year and you deserve it. Once you're done patting yourself on the back, think of a few moments where you maybe disappointed yourself, times where maybe you could've done a little bit better if you had only tried a little bit harder, or worked a little bit longer. Don't dwell on these for too long, but do recognize them. As Hannah Montana said, "Nobody's perfect. I gotta work it. Again and again till I get it right." Don't focus so much on what went wrong. Instead focus on what you can do to fix it and make Hannah Montana proud.

Finally, and this might be the hardest one of all, think about what are some things that scare you, the things that make your belly feel sick and your arms all tingly. Maybe it's heights, or maybe it's getting up at an open mic or maybe it's asking someone on a date or maybe it's werewolves under your bed. Whatever it is, if it scares you, then do it. Get on a roller coaster and see how it feels to be so up high. Take your guitar to Club Café on Monday nights and put your name on the list. Ask them out. (I don't have a solution for werewolves, they are under your bed and there's nothing any of us can do). Not only will you probably have a cool new story, it'll make you realize how easy it is to get out of your comfort zone. You just have to find the will to do it.

It's so easy to fall back into old, bad habits. You can't teach an old dog new tricks, they say. But guess what? We're not old! And we're also not dogs!! We can change our ways! We can rid ourselves of bad, dumb traits! And if that scares you, then you have to do it because I told you to. If you are already perfect and don't need to improve in any way, then ignore this whole letter. Good job.

Keep your head up and try to get over at least one tiny fear this year. If you're interested in learning more about the University of Pittsburgh chapter of the American Chemical Society (ACS) you can head to 107 Chevron Science Center. There's tons of rewarding opportunities provided through membership in ACS, so if you're reading this newsletter, you might as well check it out. Happy New Year and I wish you all a great, successful 2016!

Best,
Nuria Marquez Martinez, *Newsletter Co-Editor*

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Visit us at <http://www.chem.pitt.edu/acs-sa/>

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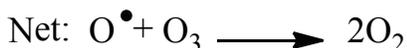
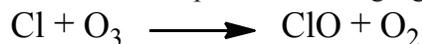
The Chemistry that Solved the Ozone Crisis

by: Jordan Leventhal, *Senior Contributor*

In May 1985 a ground-breaking paper was published in the journal *Nature* which announced the discovery of an annual depletion of ozone above the Antarctic. This depletion, referred to as the 'ozone hole,' garnered significant public attention and caused quite a stir in the scientific community as it had major implications for human health. The ozone layer in the earth's atmosphere is largely responsible for deflecting harmful ultraviolet radiation from the sun. Without it, skin cancer rates would increase significantly.

This October at the 29th Annual Kaufman Lecture, the Pitt Chemistry Department was fortunate enough to host MIT Professor Susan Solomon as she shared the story of her involvement in combatting the ozone crisis.

For Solomon it began in 1986 when she postulated the mechanism that the newly discovered Antarctic ozone hole was created by a heterogeneous reaction of ozone and chlorofluorocarbon (CFC) free radicals on the surface of ice particles in the high altitude clouds that form over Antarctica. Synthetic CFCs were commonly used in aerosol cans, air conditioning units, and refrigerators and were becoming increasingly concentrated in the atmosphere. In 1986 there were six times more CFCs in the atmosphere than natural sources of chlorine. This was a major problem because as is shown below in Solomon's postulated ozone depletion mechanism, the chlorine radicals are catalytic. This meant that very small concentrations of CFCs were capable of causing significant ozone depletion.



In order to test her hypothesis, Solomon led an expedition organized by the NOAA and NASA to Antarctica in the Winter of 1986. She and her team were able to prove that CFCs were causing the ozone hole. Subsequent studies confirmed her team's findings and in 1987 representatives from 24 nations signed the Montreal Protocol which froze CFC production at 1986 levels. In 1999 an agreement was signed in Beijing to ban global production of CFCs and today no CFCs are produced anywhere in the world.

The ozone hole over Antarctica, which was rapidly growing, has stabilized in the past ten years and scientists predict that it will disappear by the end of the century. This dramatic arrest in ozone depletion is considered to be one of the great examples of scientists, engineers and policymakers working together to solve a global environmental crisis.

Recently Solomon's research has turned to what she believes to be a more pressing and more complex environmental crisis: climate change. She is currently working to understand how to best address high variability in local climate change measurements to reveal meaningful local trends in the data. However, one thing she made very clear during her lecture is that her work is just a small piece of the puzzle. She believes that it will take global cooperation and innovation similar to what she observed during the ozone crisis to properly address climate change. Just as the ozone layer has begun to repair itself, she believes that within our lifetime global warming can be stabilized and even reversed.



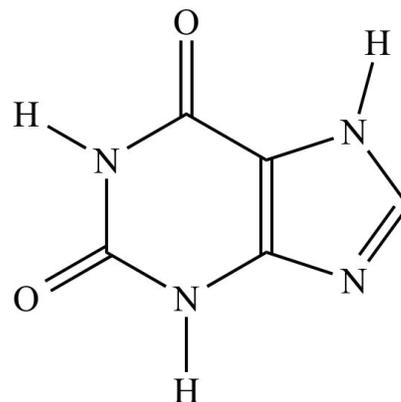
Happy
New
Year!



ALL IN THE FAMILY

by: Dan Willis, *Co-Editor*

I'm not entirely certain how to explain the link between our Chemistry Department and the skeletal formula for caffeine. I've seen it on the t-shirts, laptop cases, coffee tumblers and keychains of students all around Chevron, and it even forms the shape of the sign for our very own Bunsen Brewer. Maybe it's the fact that such a familiar chemical is paired with an equally recognizable shape—fused six- and five-member rings. Maybe it acts as a sort of esoteric badge, a prison tattoo for your Mac-Book, proclaiming, *if you know what this chemical is, you probably also used it to stay up very late and study chemicals much like it*. Or it may just have slowly become the chemical formula that people reach for when they need one to brand a product for Chemistry students. Whatever it is, it doesn't look like those handsome fused rings are going to vanish from campus any time soon.



Replacing any NHs on xanthine with NCH₃s yields one of seven

So, look at that structure over there on the right. Looks like caffeine, doesn't it? Look a little closer. That's right! In place of caffeine's three N-CH₃ bonds, that particular molecule has N-H bonds. That is xanthine, a metabolite of caffeine, and by substituting methyl groups for its amino hydrogens, any number of *methylxanthines* (of which caffeine is only one) may be produced. And of the seven theoretically possible methylxanthines, four actually occur naturally: caffeine, theobromine, theophylline and paraxanthine.

You may be wondering now how theobromine got its name despite the fact that it contains no bromine. The answer is that it is found in the seeds of *Theobroma cacao*, the tree used to make chocolate. In Greek myth, the cacao tree was bestowed upon humans by gods during a time of extreme hardship. Hence, chocolate is Theobroma, or the "food of the gods" (from *theos*, meaning 'god' as in 'theology' and *broma*, meaning 'food' as in the medical term for starvation 'abrosia'). But it's not just theobromine that's in chocolate, and it's not just chocolate that contains theobromine. In fact, almost every food or drink with which we associate energizing properties contains some cocktail of methylxanthines. That includes not just chocolate and coffee, but also tea, kola, guarana and ginseng.

But there is only one significant botanical source of all four methylxanthines, and it's a mysterious tree from South America called Yerba Mate (pronounced YUR-buh MAH-tay). Actually a part of the holly family (hope you had a wonderful holiday season, by the way), the leaves of this tree are brewed into a tea that has been popular in South America since the 16th century, so popular that it's been declared the official national beverage of both Argentina and Paraguay. It may be served hot or cold, sweetened or unsweetened, the taste is woody and bitter and the purported health effects have helped its profile in North America grow considerably in recent years. It's not hard to find in tea shops, health food stores and even the occasional gas station.

So root for the underdog! Coffee and caffeine are great, but try getting your kick elsewhere; go for a new beverage with a whole new chemical profile! At the very least, next time you see that ubiquitous icon, the caffeine structure, give some of the other methylxanthines some credit. They too can be the food of the gods.

References:

<http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3820066/>

<http://www.britannica.com/topic/mate-beverage>



*The University of Pittsburgh
Department of Chemistry*

is proud to announce

*The Wass and McKeever Summer
Undergraduate
Research Fellowships*

- **T**he Undergraduate Research Fellowships will be awarded this Summer, 2014.
- **T**his Fellowships will provide a Summer stipend of \$3,500.00 to the recipient for work carried out in the research lab of our faculty member.
- **P**lease submit a letter of recommendation from a Faculty Mentor which includes your qualifications and details of the planned research project (1-2 pages) and a **one** page personal statement of your future goals to **Dr. George C. Bandik in Room 107 Chevron Science Center by February 20, 2016**. All nominations will be reviewed by our Undergraduate Curriculum Committee and the recipient will be recognized at our Undergraduate Spring Term Awards Ceremony within the University of Pittsburgh, Department of Chemistry.

Deadline to receive all materials for both Fellowships is February 20, 2016.



The Department of Chemistry of the University of Pittsburgh and The Valspar Corporation

are pleased to announce

The Valspar Corporation Award in Chemistry

The Award will be made in Spring 2016 to one or more outstanding chemistry majors completing their sophomore or junior year. The award consists of a three month paid internship for Summer 2016 in the Valspar Laboratories in Pittsburgh, plus a \$2,000 scholarship to be used to attend the University of Pittsburgh during the student's junior or senior year.

Criteria for the award are as follows:

- a) The student must be a non pre-professional chemistry major at the University of Pittsburgh.
- b) The student must have a 3.0 or higher grade point average at the time of selection.
- c) Where applicable, financial need will be considered.

To apply for the award:

- 1) Complete and submit an application form (available in 107 Chevron Science Center).
- 2) Submit an unofficial transcript of all undergraduate work.
- 3) Arrange for a letter of reference (from a member of the University of Pittsburgh faculty) to be submitted.

Materials are to be submitted to:

Dr. George C. Bandik
107 Chevron Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

**Deadline for all application materials is
January 27, 2016**

2016 January ACS-SA Schedule

08 NO MEETING

15 Officer's Meeting

22 Valspar Corporation

Kevin Romagnoli, B.S.

University of Pittsburgh

Department of Chemistry Graduate

29 Welcome Back Party

Reservations REQUIRED

Hoagies and Sample Exams yet Again!

Our most visible activities are the ACS hoagie and Chemistry Exam sales. Just about everyone having a Chemistry Lab class in Chevron has at one time or another eaten an ACS hoagie from Uncle Sam's while studying. The funds raised by these sales help to defray the weekly meeting expenses for refreshments and other incidentals as well as the cost of the food and supplies at our social functions.

Hoagies are sold on Tuesdays throughout the semester.



I Need a Job!

It's that time of year! Time to begin the search for a summer position. There are several opportunities for summer opportunities available to Chemistry majors.

The first place to look is the Chem Major News area of the first floor hallway. Here you will find the current Research Experiences for Undergraduate (REU) listings. They are from all over the country.

You may also want to visit Career Services (2nd floor WPU).

Ms. Emily Bennett can help you with opportunities available through their Office.

Finally, don't forget the Arts and Sciences Office of Experiential Learning (B-4, Thaw Hall). Mr. Patrick Mullen can assist you there.

With all of these opportunities available, it should be an exciting and productive summer for everyone. Good Luck!



Green Chemistry

by: Viktor Polites-Green Chemistry Contributor, 2015-2016



Greener Approaches to Alcohol Oxidations

Much of organic chemistry research is devoted to pioneering novel reactions which achieve carbon—carbon bond formation. However, functional group transformations (e.g. oxidation, reduction, halogenation) are equally important for they are used to access derivatives to be used for carbon—carbon bond-forming reactions. Alcohol oxidations to ketones, aldehydes, and carboxylic acids in particular represent a challenge for green chemistry since they require a stoichiometric sacrificial reagent, and the first choice of reagent has for long been some form hexavalent chromium, a known human carcinogen.¹

The danger of chromium is averted by using oxidation protocols such as the Swern oxidation,² or Dess-Martin Periodinane (DMP).³ However, they also have their drawbacks. The Swern oxidation produces the toxic compounds dimethyl sulfide and carbon monoxide as by-products. The drawback of DMP (Fig. 1) is the high molecular weight (424.14 g/mol) of the sacrificial oxidant. As a result, the procedure has inherently dreadful atom economy, particularly when doing oxidations on low molecular weight alcohols.

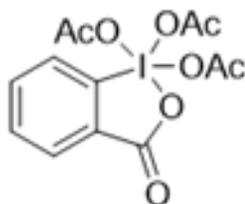
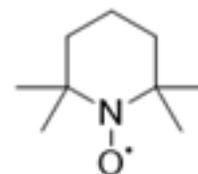


Figure 2. Dess-Martin Periodinane

One particular “green” approach to doing alcohol oxidations which has gained traction uses catalytic quantities of an oxoammonium salt or its precursor nitroxyl radical, the most commonly used of which is 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, Fig. 2). Anelli and co-workers published a landmark paper in 1987 in which MeO-TEMPO



turnover was achieved under relatively mild conditions using stoichiometric sodium hypochlorite, or bleach, the dual-solvent system dichloromethane and slightly basic aqueous buffer. Primary alcohols are rapidly oxidized to aldehydes, with slow carboxylic acid formation. The acid can be obtained rapidly by adding a phase-transfer catalyst.⁴ In 1999, Zhao et. al. expanded the utility of the procedure to substrates sensitive to chlorination by hypochlorite. They reduced the hypochlorite loading to catalytic quantities and used sodium chlorite as the sacrificial oxidant.⁵

Figure 2. TEMPO

Recently, the Stahl group at the University of Wisconsin—Madison have been exploring nitroxyl radical systems for alcohol oxidations which use air as the terminal oxidant. To selectively oxidize primary alcohols, particularly allylic and benzylic alcohols, the group employed the catalyst ensemble of TEMPO, N-methylimidazole (NMI), CuOTf, and 2,2'-bipyridine (bpy).⁶ To oxidize primary and secondary aliphatic alcohols, the group employed the more reactive catalyst 9-azabicyclo[3.3.1]nonane N-oxyl (ABNO) instead of TEMPO.⁷ Both processes have been used effectively on process scale in batch reactors and in flow reactors.⁷⁻⁸

In conclusion, the lack of a truly “green” protocol for alcohol oxidations, a routine transformation for organic synthesis, has been long overlooked. Procedures that don't use chromium oxidants such as DMP and the Swern oxidation are an improvement since the reagents are not carcinogenic by inhalation. The most “green” procedures use innocuous, inorganic terminal oxidants such as bleach or oxygen, and catalytic oxoammonium species (from the nitroxyl radicals TEMPO or ABNO) as the active oxidant. These protocols have the added benefits of being relatively mild reaction conditions, and affording tunable selectivity for aldehyde or carboxylic acid formation from primary alcohols, and tunable selectivity for alcohols based on steric and electronic considerations.

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American Chemical Society

Student Affiliates, University of Pittsburgh

Membership Application

This is a powerful professional organization for the benefit of individuals interested in chemistry and related fields. Our organization offers exciting extracurricular activities and many outstanding opportunities for our members, including:

- 1 WEEKLY MEETINGS**-to plan activities, provide interesting speakers, discuss ideas, and keep students aware of what is happening in the scientific community.
- 2 ANNUAL TRIPS**-Each year we sponsor (a) trip(s), to external chemistry environments, as well as for social enjoyment. Significantly reduced rates are available to active members. In the past few years we have traveled to New Orleans, Atlanta and New York.
- 3 PROFESSIONAL NETWORKING**-Our organization has many opportunities to make contacts with professionals in both the scientific industry and academia. Student affiliates also have the opportunity to join the National ACS.
- 4 SOCIAL ACTIVITIES**-We sponsor many activities throughout the year just for fun.

Our meetings are held every Friday at 12:00 noon in Room 135 Chevron Science Center. To join, complete the application form below and come to one of our meetings. Our first meeting will be January 15, 2016 but you may join any time throughout the year.

Name: _____
School Address: _____ _____
Permanent Address: _____ _____
School Phone: _____ Home Phone: _____
Major: _____ Year in School Fr. So. Jr. Sr.
E-mail: _____
May we include your name, number and e-mail on the published phone list? YES NO

To submit this form by mail, send it to ACS-SA, Box 24, Chevron Science Center, University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260. Be sure to include the \$15.00 dues (make checks payable to the University of Pittsburgh). It is possible to be active even if you can not attend the meetings. For more information, see our display case in the lobby of Chevron Science Center.

