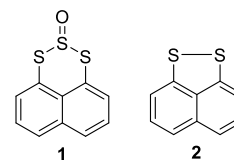


PRF Grant: 57667-ND3
Project Title: Sulfur and Selenium Monoxide Transfer Reagents
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INTRODUCTION

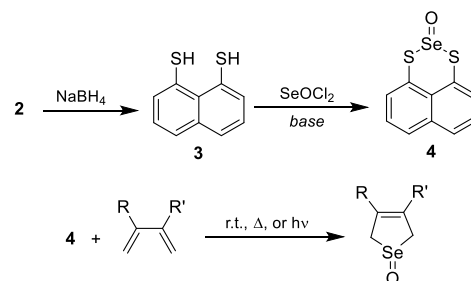
The overarching goal of our PRF-funded work is the development of new main-group inorganic chemistry, specifically the incorporation of sulfur monoxide (SO) and selenium monoxide (SeO) into organic and inorganic molecules. Both these diatomic molecules are unstable and so need to be generated in-situ. Some precedent exists for preparative chemistry involving sulfur monoxide, the SO being generated by extrusion from organic molecules or from transfer from inorganic complexes. The Grainger group in Birmingham has previously prepared and used SO transfer agent **1**. It is generated from disulfide **2**. Selenium monoxide has not been used synthetically and a practical method for its generation is not known. Our objectives are: (1) to develop novel SO transfer reagents, (2) to probe the chemistry of SO with inorganic and organometallic compounds, and (3) prepare an SeO transfer reagent. The project involves students at both the University of Connecticut and the University of Birmingham. In this first year of the funding period, a graduate student from Connecticut spent a period of a month working with the Birmingham group.



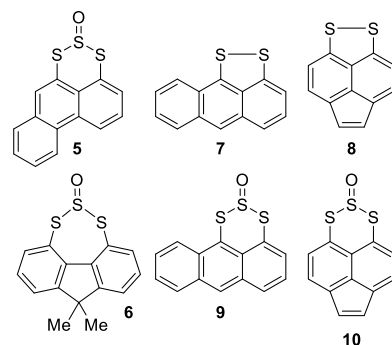
RESEARCH PROGRESS

In Connecticut, we have focused most of our attention on developing a route to a selenium monoxide transfer agent using **2** as a backbone. To achieve this, we first tried to devise an improved synthesis of disulfide **2**. This compound is traditionally prepared from naphthalene using a significant excess of *n*-butyllithium and results in only moderate yields of **2**. Despite attempting a number of novel alternative synthetic strategies for preparing **2**, we were unable to generate the target compound in yields that were higher than the original route.

To prepare an SeO transfer agent, we followed an analogous route to that used by the Grainger group to generate **1** from **2**. Treatment of disulfide **2** with sodium borohydride yielded dithiol **3**. Adding selenium oxychloride to a solution of **3** gave what we believe to be SeO-containing compound **4**. Unlike its sulfur analog **2**, we find that **4** is unstable at room temperature. This affects the yield of the reaction to generate **4**, as well as its definitive characterization and ultimately its potential use as an SeO transfer agent. We have probed the identity of **4** using a combination of infrared, mass, and ¹H-, ¹³C- and ⁷⁷Se-NMR spectroscopy. Data is in line with what would be expected for our proposed structure. We are currently attempting to obtain single crystals of **4** for definitive characterization of the compound. We have also performed a series of experiments directed around extruding and trapping SeO. Attention has focused on in-situ trapping using dienes to yield selenoxides, performing the reactions at room temperature, elevated temperature, and photochemically. To date we have not had success in this endeavor, but do see the formation of selenium dioxide in the reactions. This, and the observation that the reaction of **4** with triphenylphosphine generates triphenylphosphine selenide (Ph₃P=Se), provides evidence for the presence of a selenium moiety in **4**. We have performed a series of molecular modeling calculations to probe computationally the extrusion of SO and SeO from a variety of backbone structures to aid in next steps of the project. Experimentally, we are continuing to explore the reaction chemistry of **4**. Alongside this, we are currently exploring preparing other backbones for the subsequent generation of SeO transfer agents, as well as embarking on a study of the reaction chemistry of **1** with metal complexes so as to initiate work on proposal objective 2.



In Birmingham, attention has focused on developing new backbones for use in sulfur monoxide transfer. We have prepared the phenanthrene trisulfide-2-oxide **5**, and shown it to have very similar reactivity to **1** in thermal and photochemical SO transfer to dienes. We have also, very recently, successfully prepared fluorene trisulfide-2-oxide **6**, and will now initiate studies into its reactivity. Difficulties in the synthesis of disulfides **7** and **8** have meant we have as yet been unable to attempt their conversion to the potential corresponding SO transfer reagents, anthracene trisulfide-2-oxide **9** and phenanthrene trisulfide-2-oxide **10**. Synthesis of more accessible derivatives of **8** towards analogs of **10** which retain the desired structural and electronic features for SO transfer is currently under investigation.



IMPACT OF THE RESEARCH

The funded project has allowed the Connecticut and Birmingham groups to participate in a formal international collaboration and we hope that with some preliminary results in hand we can apply for further jointly funded research through channels such as the US National Science Foundation and the UK Engineering and Physical Sciences Research Council, as well as student exchange programs funded through the Universitas 21 framework, of which both our institutions are a part.

The project has funded a University of Connecticut graduate student (Shelli Miller) to work on the project during the 2017-18 academic year as well as the summer of 2018. An undergraduate exchange student from the University of Edinburgh in the UK (Kathryn Bisset) has been involved in aspects of the work and was directly supervised by Shelli. Two other undergraduate students were co-supervised by Shelli and another graduate student in the Connecticut research group and participated in some of the reactions funded by the grant. The funded work has not only exposed the undergraduate students to common organic chemistry techniques, but also allowed them to gain experience handling air and moisture sensitive compounds and analyzing reaction mixtures to characterize products. In Birmingham, a graduate student (Connor Prior) and a postdoctoral fellow (Dr. Ian Pocock) worked on the project, being funded by the UK Leverhulme Trust through a Ph.D. studentship and postdoctoral fellowship, respectively. Shelli spent a month over the summer at the University of Birmingham working together with Connor, sharing the approach she developed for the preparation of **4** as well as working together on novel backbone synthesis. This was Shelli's first time outside the United States and greatly broadened her horizons. She was able to expand her professional and personal networks, and her knowledge of cultures different from her own. A reciprocal one-month visit of Connor to the University of Connecticut is being planned to take place in March 2019.