9-1-2020

Diphenyl ditelluride: An inorganic laboratory exercise featuring a main group organometallic target

Maggie Ludwig
Winona State University

Joseph West
Winona State University

WINONA STATE UNIVERSITY
TRAVEL SUPPORT FOR UNDERGRADUATE STUDENT RESEARCH & CREATIVE PRESENTATIONS
FINAL REPORT

Submit this complete form and a copy of the project end product(s) no later than ten (10) days after the conclusion of travel. Submit items as attachments to the WarriorSpace Travel Support for Undergraduate Student Research & Creative Presentations form that you used to submit your application.

For more information, go to the Student Grants webpage.

Final Report Checklist

The final report **MUST** include this form and the end product(s) (*check to verify inclusion of each component*):

- [x] This final report fully completed
- [x] A copy of the project end product(s). Indicate the format of your final product(s) (*select all that apply*):
  - [ ] Research Report
  - [ ] Presentation
  - [x] Poster
  - [ ] Other – Please describe:

Note: A copy of the project end product will be forwarded to Krueger Library for archival purposes.

Project Information

Title of Project: Diphenyl ditelluride: An inorganic laboratory exercise featuring a main group organometallic target	
Student Name (Lead): Maggie Ludwig	Student Email: Maggie.Ludwig@go.winona.edu
Co-Investigators Names: None	
Faculty Sponsor: West, Joseph K	Faculty Department: CHEMISTRY
Date of Presentation: 4/5/2021	Location of Conference: Online or Virtual Event
Event Name: National ACS Spring 2021 Meeting	
Was this a capstone, senior thesis, or other degree culminating project? No	

Project Abstract

While there are many organometallic complexes that are commonly used as synthetic targets for upper-level inorganic chemistry courses, those utilizing p-block metals are quite rare. We have designed an expeditious procedure to prepare diphenyl ditelluride that can be fully completed in a 4-hour laboratory period. This laboratory exercise can serve as a transition between the organic and inorganic curriculum, an introduction to the handling of air-/moisture-sensitive substances and reintroduction to several critical laboratory skills. Students completed characterization of their products via melting point, UV-vis spectroscopy, mass spectrometry, and multinuclear NMR. An additional molecular modeling supplement has been designed to facilitate exploration of the effects of atomic size and propensity towards hybridization on observable structural parameters for related dichalcogenides.

Diphenyl ditelluride: An inorganic laboratory exercise featuring a main group organometallic target

Maggie Ludwig and Dr. Joseph K. West

Chemistry Department, Winona State University

Abstract

While there are many organometallic complexes that are commonly used as synthetic targets for upper-level inorganic chemistry courses, those utilizing p-block metals are quite rare. We have designed an expeditious procedure to prepare diphenyl ditelluride that can be fully completed in a 4-hour laboratory period. This laboratory exercise can serve as a transition between the organic and inorganic curriculum, an introduction to the handling of air-/moisture-sensitive substances and reintroduction to several critical laboratory skills. Students completed characterization of their products via melting point, UV-vis spectroscopy, mass spectrometry, and multinuclear NMR (^{125}Te{^{1}H}, ^{13}C{^{1}H}, and ^{1}H). An additional molecular modeling supplement has been designed to facilitate exploration of the effects of atomic size and propensity towards hybridization on observable structural parameters for related dichalcogenides.

Introduction

Synthesis labs rarely feature the heavy main group elements. In part due to their toxicity, less stable molecular compounds, and relative lack of applications, the p-block metals have received less attention than their d-block counterparts. Organotellurium compounds are becoming more prevalent, with applications in medicinal chemistry and synthetic organic chemistry continuously on the rise.

With this in mind, we sought to develop a synthesis-based lab targeting diphenyl ditelluride. Traditional synthesis reports for diphenyl ditelluride involve several distinct steps and require multiple multi-hour refluxes and an extensive work-up procedure that would require 2–3 full laboratory sessions to complete. As such, our main goals for this project were to 1) significantly shorten the procedure to fit most, if not all, into a single lab session, and 2) develop a fool-proof procedure that has been thoroughly tested and should be easily reproduced by students that have completed the prerequisite organic chemistry sequence.

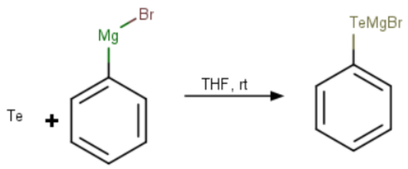
References

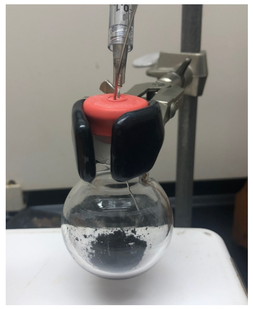
(1) Engman, Lars; J. *et al. J. Organomet. Chem.* **1990**, *388*, 71–74.
(2) Singh, Devender *et al. Org. Lett.* **2010**, *12*, 3288–3291.
(3) Koellemann, Christoph *et al. Organometallics* **1991**, *10*, 2101–2102.
(4) Spencer, Liam P; *Inorg. Chem.* **2009**, *48*, 2693–2700.
(5) J.S. Gordon *et al. J. Comput. Chem.* **1993**, *14*, 1347–1363.

Objectives and Approach

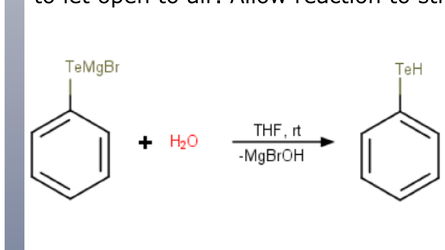
A 25 mL three neck, round bottom flask was oven dried for at least 30 minutes prior to experiment. 638 mg of tellurium was added to flask along with a small stir bar. The flask was sealed with a septum and purged with nitrogen for 5 minutes.

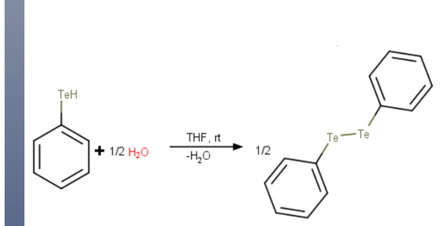
Using a nitrogen filled needle and syringe, 1.0 M phenylmagnesium bromide/THF solution was measured out. At room temperature, with stirring, Grignard solution was added dropwise over 10 minutes.





Wait 10 minutes after the addition and remove the septum to let open to air. Allow reaction to stir open-air for 1 hour.

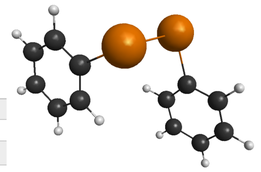




For product workup, THF was evaporated by replacing septum and pulling vacuum through needle. Rotary evaporator could alternatively be used to speed up the process. Once dry, ~10 mL of hexanes was added and swirled to dissolve product. A glass frit and ~1.5-2 cm of Celite was used to filter suspension and unreacted Te. To wash product through frit, up to 10 mL of hexanes was used. The hexanes solution was transferred into pre-weighed vial and evaporated at room temperature for a week. For recrystallization, product was dissolved in warm hexanes followed by submersion in an ice-salt bath. Crystals were filtered using a Hirsch funnel and air dried.

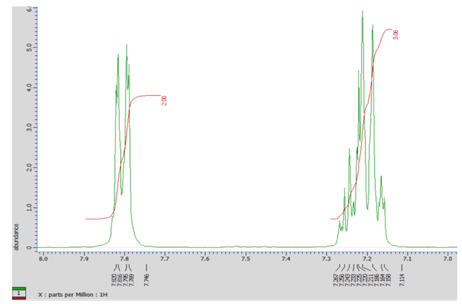
Modeling

Ph_2E_2 (E=)	Bond Length (Å)	CEE Angle (-°)
S	2.27557	100.8
Se	2.48483	99.94
Te	2.87561	97.71

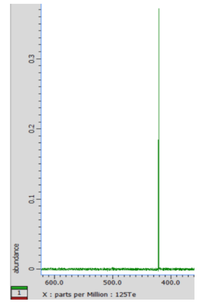


As a supplemental exploration of bonding trends through structure, diphenyl dichalcogenides were modeled. The decreasing degree of hybridization upon descending the group is made apparent by the reducing CEE bond angle. All structures were modeled in GAMESS at the HF/3–21G level of theory.

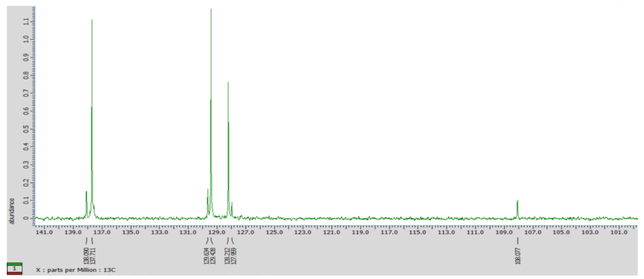
Characterization



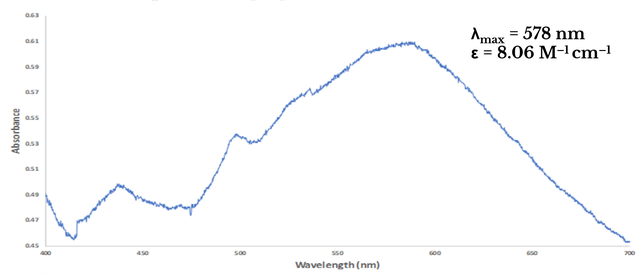
^{1}H NMR Spectrum of Ph_2Te_2



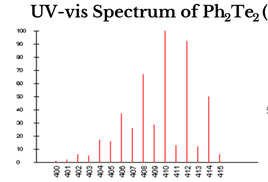
^{125}Te{^{1}H} NMR of Ph_2Te_2



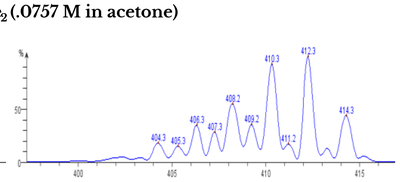
^{13}C {^{1}H} NMR Spectrum Ph_2Te_2



UV-vis Spectrum of Ph_2Te_2 (.0757 M in acetone)



Predicted MS of Ph_2Te_2



Experimental MS of Ph_2Te_2

Discussion and Conclusion

After comparing our experimental data with literature reports we have verified our approach to be not only faster, but also providing a slightly improved yield of 74.2% (typical literature yields range from 68–72%, for this general route). Experimental melting point of 60–61°C is similar to literature values of 64–65°C (different solvents were used)[1]. NMR spectra were also correlated to literature spectra [2-4].

We worked toward developing a faster route to the compound diphenyl ditelluride and shortened the procedure to fit into one lab session. This lab serves to combine organic synthesis procedures in order to use the lab as a "bridge" between this course and the organic chemistry prerequisite.

Future Work

Future expansions to this lab will most likely involve application tests, such as 1) standardization of an alkyl lithium solution, 2) preparation of other organotellurium compounds, and/or 3) bioactivity assessment(s).

A side product of diphenyl telluride was observed in the ^{13}C{^{1}H} and ^{125}Te{^{1}H} NMR spectra of the crude product. This is especially surprising considering all reports for its synthesis utilize very different approaches. A logical progression given this observation is to attempt to favor its formation through changes in reactant stoichiometry and conditions.

The currently proposed workup for isolation of the product is lengthy and includes multiple steps. In an effort to further quicken the procedure, an improved workup and isolation protocol may be developed.

Acknowledgements

Thank you, Dr. West, for guiding me on this project and patiently handling every roadblock that came with it. Also, I would like to thank the Winona State University Chemistry department, for letting me use its resources and lab space.

Presenter email: maggie.ludwig@go.winona.edu

Diphenyl ditelluride: An inorganic laboratory exercise featuring a main group organometallic target

While there are many organometallic complexes that are commonly used as synthetic targets for upper-level inorganic chemistry courses, those utilizing p-block metals are quite rare. We have designed an expeditious procedure to prepare diphenyl ditelluride that can be fully completed in a 4-hour laboratory period. This laboratory exercise can serve as a transition between the organic and inorganic curriculum, an introduction to the handling of air-/moisture-sensitive substances and reintroduction to several critical laboratory skills. Students completed characterization of their products via melting point, UV-vis spectroscopy, mass spectrometry, and multinuclear NMR ($^{125}Te\{^{1}H\}$, $^{13}C\{^{1}H\}$, and ^{1}H). An additional molecular modeling supplement has been designed to facilitate exploration of the effects of atomic size and propensity towards hybridization on observable structural parameters for related dichalcogenides.

Maggie Ludwig and Dr. Joseph K. West
Chemistry Department, Winona State University