

## Introduction

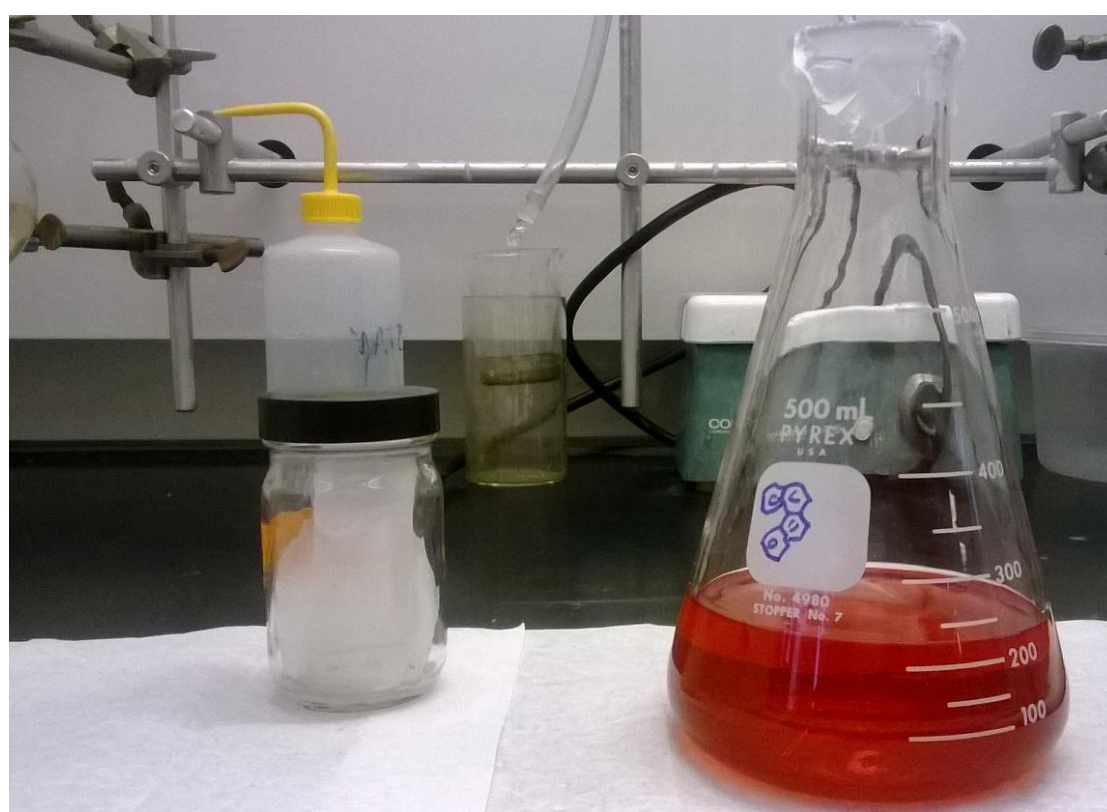
Benzo[c]phenanthrene (**1**) is a polycyclic aromatic hydrocarbon commonly found as a combustion byproduct. **1** exists as a yellow solid when purified.<sup>1</sup> Absorbance in visible spectrum is caused extensive conjugation and delocalization of both the HOMO and LUMO orbitals, decreasing the band gap into the near visible region. The calculated UV/VIS absorbance spectrum is also shown in Figure 3.

Formation **1** is hypothesized to be a radical process, on which small carbon based radicals (C2,C3) add to larger rings.<sup>2</sup> Collectively molecules similar to

**1** coagulate together to form soot, which is thought to contain polycyclic aromatic hydrocarbons with a molecular weight exceeding 500 amu.<sup>3</sup>

PAH's are of interest due to their ubiquity as an atmospheric pollutant via their production in all types of combustion. PAH's have shown serious mutagenic properties, with the oxo and nitro<sup>4</sup> derivatives binding quite easily to DNA. PAH's affect early childhood development, with children exposed to higher levels of PAH's exhibiting lower overall IQ.<sup>5</sup> Prenatal exposure has also been detrimental.

Aliphatic fuels devoid of aromatic compounds are hypothesized to form PAH's from fuel decomposition products, with acetylene radicals being the primary route of production.<sup>6</sup>

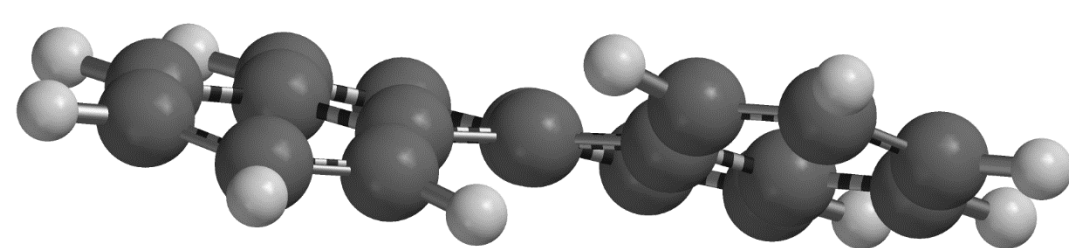


*Benzo[c]phenanthrene pre purification & iodine removal.*

## Calculated Graphics

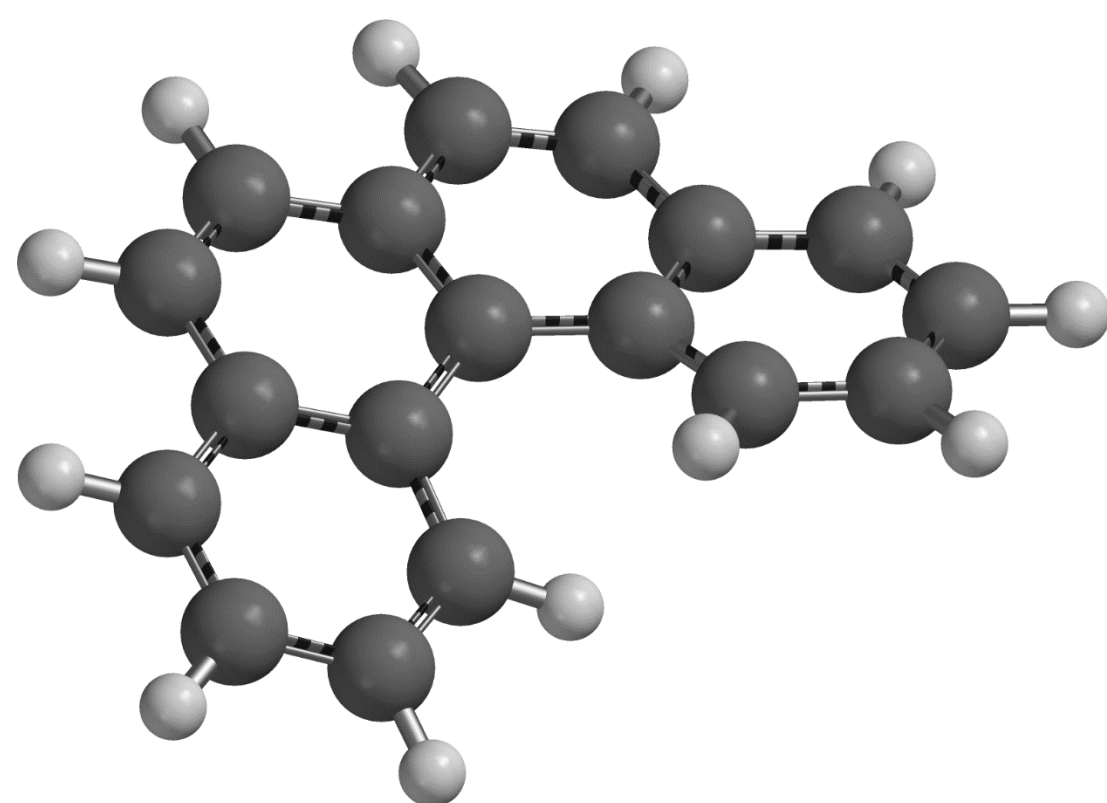
*Calculations were completed with Spartan 10, B3LYP/6-311G\* level of theory.*

Figure 1



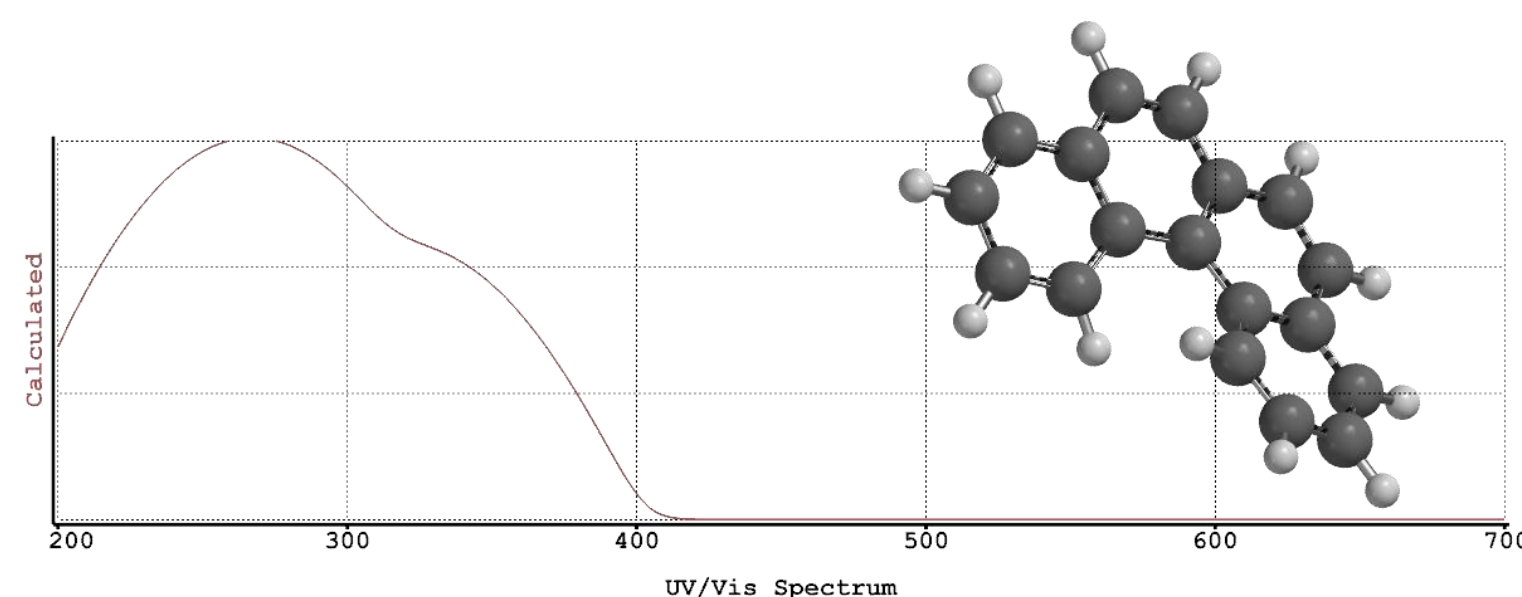
The helical structure of benzo[c]phenanthrene results in **1** being chiral through the configuration of the helix. **1** exists in both *M* and *P* helicity. An alternative name for **1** is tetrahelicene.

Figure 2



Benzo[c]phenanthrene gets its systematic name by simply adding benzene to the "c" bond of phenanthrene.

Figure 3



UV/VIS Spectra of **1** shows absorbance in the ultraviolet in to the far visible spectrum. An absorbance in violet would result in the complimentary color, yellow, being transmitted.

## Conclusions

Reaction 1 was successful in low yield, which could be mediated by using a different base to deprotonate the Wittig reagent, benzyltriphenylphosphonium chloride. A base, such as n-butyllithium could be used to achieve a greater fraction of deprotonation and thus more activated Wittig reagent. If the reaction is repeated to generate more **1** n-butyllithium will be used. A solvent system was also worked out for the purification of the intermediate **2** which will be useful for future syntheses.

There is currently no data available on reaction two, as this will be updated as data is generated. Reaction is completed, but must undergo column chromatography via the CombiFlash.

## Future Work

**1** will undergo Vacuum Flash Pyrolysis in tandem with a hydrogen atom donor to investigate possible radical catalyzed rearrangements of **1** to it's isomers: Benzo[a]anthracene, tetracene and chrysene.

A computational model of the interconversion between the benzo[c]phenanthrene isomers will be developed based on B3LYP/6-311G\* theory.

## Acknowledgements

Thanks to Sarah Joiner for logistical assistance, chemical expertise, assistance using the CombiFlash and tons of NMR runs, thanks to Dr. Johnson for allowing the use of his lab and allowing the use of his CombiFlash, and thanks to Hillary Thompson for assisting me when Sarah was out of reach.



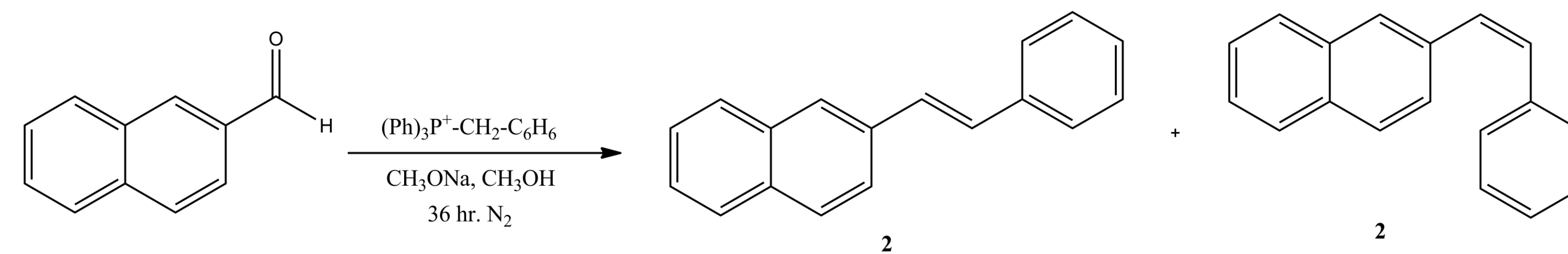
# Synthesis of Benzo[c]phenanthrene

Tyler Dami

Department of Chemistry, University of New Hampshire, Durham NH  
11/29/13

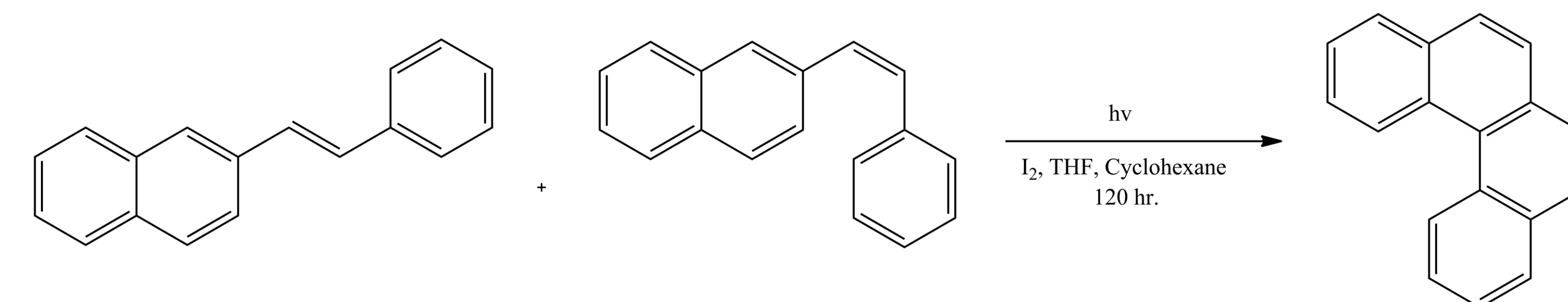
## Scheme

Reaction 1



*Reaction was performed under nitrogen atmosphere, with constant agitation. 7% product yield.*

Reaction 2



*Reaction was performed in three 100mL quartz tubes in photoreactor for 120 hrs.<sup>1</sup>*

## Results and Discussion

The production of **1** has proven to be a synthetic challenge, although the procedure was available in the literature many of the steps were ill defined. Reaction 1 produced 7% of the expected yield, this was, however, enough to proceed with reaction two. Reaction two is waiting purification to determine a yield, and will be reported at a later date.

Reaction 1 goes to product through a standard Wittig mechanism, in which a cyclobutyl intermediate is produced. The intermediate collapses into the more thermodynamically stable carbon – carbon and carbon-phosphorus bonds.

Reaction 2 goes from stilbene derivative

to product via a 6 electron photochemical electrocyclic ring closure. Photochemical cis-trans isomerization ensures the correct isomer is generated. According to Woodward Hoffman rules this electrocyclic reaction results in a Conrotatory ring closure. This followed by the loss of both a proton and a hydride restores aromaticity to the system. HI is produced as a byproduct and neutralized by the THF in situ via acid catalyzed ether cleavage.

Literature reports 31% yield for reaction 2 after a reaction time of 36 hrs. A longer reaction time was chosen to examine the possibility of a greater yield due to the longer exposure to UV lamps.

The final product is awaiting purification via the CombiFlash, crude yield is 70%



*The CombiFlash, an automated column chromatography unit with inline UV/VIS spectral analysis.*

## References

1. Talele, Harish R., et al. Expeditious synthesis of helicenes using an improved protocol of photocyclodehydrogenation of stilbenes. *ARKIVOC*. **2011**, 9, 15-37.
2. Richter, Henning, William J. Grieco, and Jack B. Howard. Formation mechanism of polycyclic aromatic hydrocarbons and fullerenes in premixed benzene flames. *Combustion and Flame*. **1999**, 119.1,1-22.
3. Richter, H., and J. B. Howard. Formation of polycyclic aromatic hydrocarbons and their growth to soot—a review of chemical reaction pathways. *Progress in Energy and Combustion Science*. **2000**, 26.4, 565-608.
4. Pitts, J. N., et al. Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. *Science*. **1978** 202.4367, 515-519.
5. Perera, Frederica P., et al. Prenatal airborne polycyclic aromatic hydrocarbon exposure and child IQ at age 5 years. *Pediatrics*, **2009** , 124.2 , 195-202.
6. Atkinson, Roger, and Janet Arey. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens. *Environmental Health Perspectives*. **1994**, 102 , 4116-4117.