Organic Chemistry Final:
Complete Mechanism for the Synthesis of [7]Circulene

Cade Reinberger

Cincinnati Hills Christian Academy

July 31, 2020

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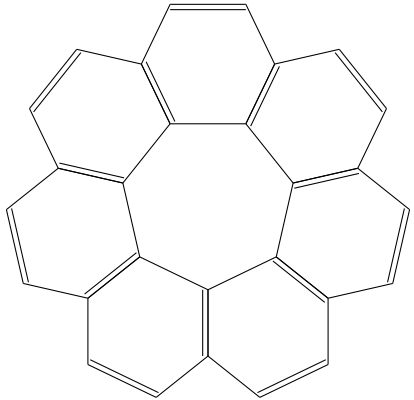
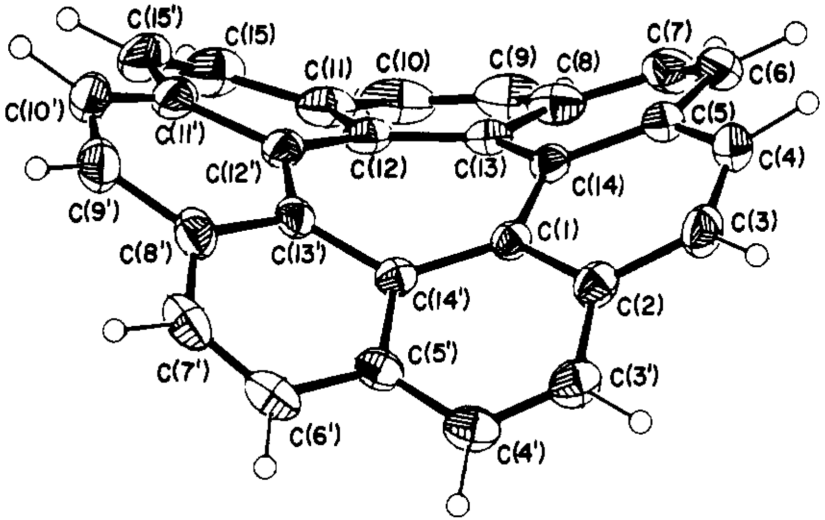
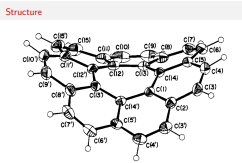


[7]Circulene

- Polyaromatic Hydrocarbons ($\approx$ graphene derivatives) are of interest to materials scientists for their electrical properties. Applications like Organic Field-Electron Transistors, and organic photo-voltaic cells. These are of increasing value. [**Newswire**]
- Base-level research in these contorted and geodesic polyarenes are therefore important, and that's a key purpose of molecules like circulen–in the understading of syntheses and reactions of these types of compounds.

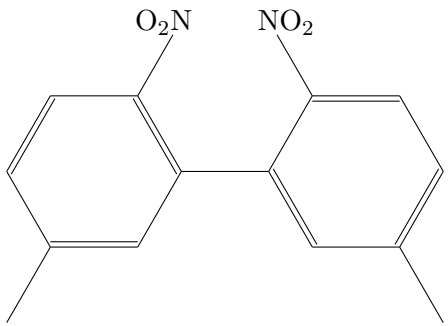
Structure



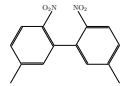


- X-Ray Crystalography shows, shockingly, that the symmetry group is isomorphic to $\mathbb{Z}_2$!
- Why would there be contortion? It seems, intuitively that the strain effects, especially for just a 7-membered ring, wouldn't have the same order of magnitude as the effects of stability added when perfectly planar. The answer, digging in to the computer calculation, is twofold. Partly, the resonance stabilization decreases less than you might expect. Partly that's the nature of MO's and linear combination of basis states, but also there's some intuition–think of our dibenzalacetone lab. But, also the ring strain effects add up. There are like 14 involved bonds, so you pick up an order of magnitude in calculation of the strain energy. [**Karadakov**]

Starting Compound: *5,5'–dimethyl–2,2'–dinitrobiphenyl*

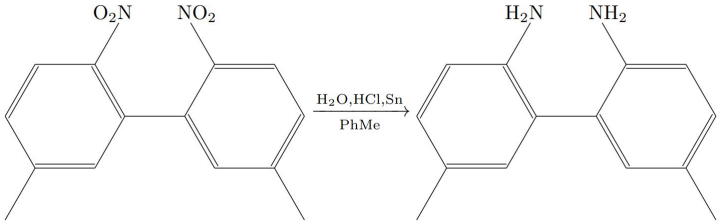


Starting Compound: *5,5'–dimethyl–2,2'–dinitrobiphenyl*



- Toluene is found in nature, and a byprodct of several key industrial processes, gasoline cracking and the production of steel from coke. Biphenyls are prepared by certain coupling reactions, thereof, so di-methyl-biphenyls are quite natural to work with [**Ullman**]
- Nitration of aromatic compounds has a resonance, and this makes it one of the most common and well-studied among electrophilic aromatic substitutions, which mikes the Nitro compound also a good starting point. [**Smith**]
- Since the steps of EAS and coupling reactions yield differently directed compounds, it's also far cheaper to buy this as a starting point from a company that will sell other isomers than to synthesize.

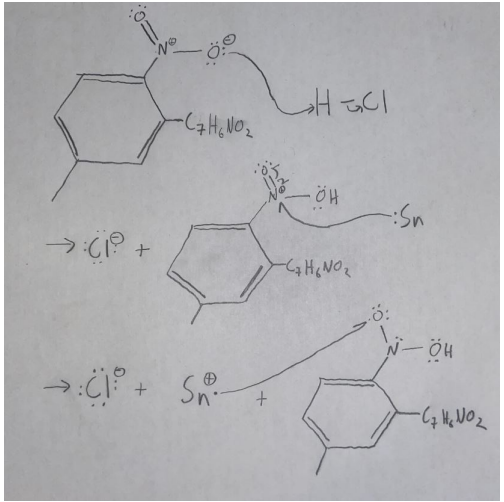
Reduction of Aromatic Nitro Groups



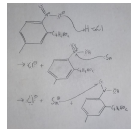
Reduction of Aromatic Nitro Groups

- Tin Catalysis with SET–industrially actually want excess of 6 equivalents of Sn. Why? Roughly, Tin has first Ionization energy 708.6 kJ/mol and second ionization energy 1411.8 kJ/mol, so it's usually cheaper to just improve the efficiency and lower the activation energy just by shelling out for the extra equivalents of Tin.
- Single Electron transfer is a special case of a radical mechanism. In the same way that an Sn2 is a special case of a non radical reaction. You can think of it roughly as a radical nucleophilic attack.

Reduction of Aromatic Nitro Groups: Mechanism #1

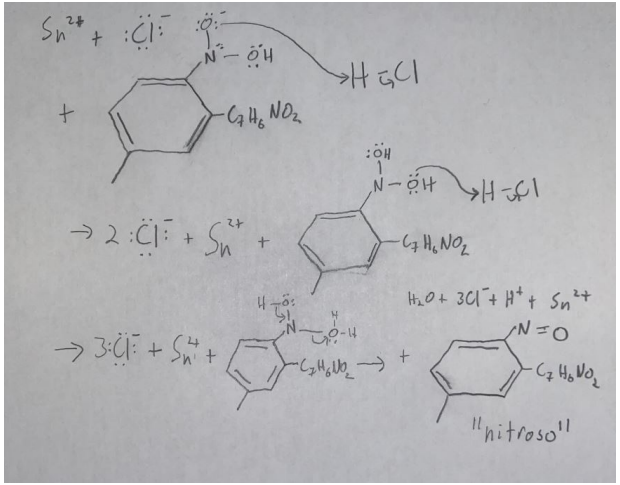


Reduction of Aromatic Nitro Groups: Mechanism #1

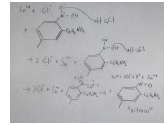


- attack of the Sn fundamentally nucleophilic though radical.
- second attack could could come from first radical of second Sn if 6 equivalents per nitro. This distinction illustrates SET vs simple nucleophilic attack.
- Though not neccessary, for this first reaction only, since it's so complicated and the equivalents thing is illustrative of the mechanism, we will keep track of all compounds once used.

Reduction of Aromatic Nitro Groups: Mechanism #2

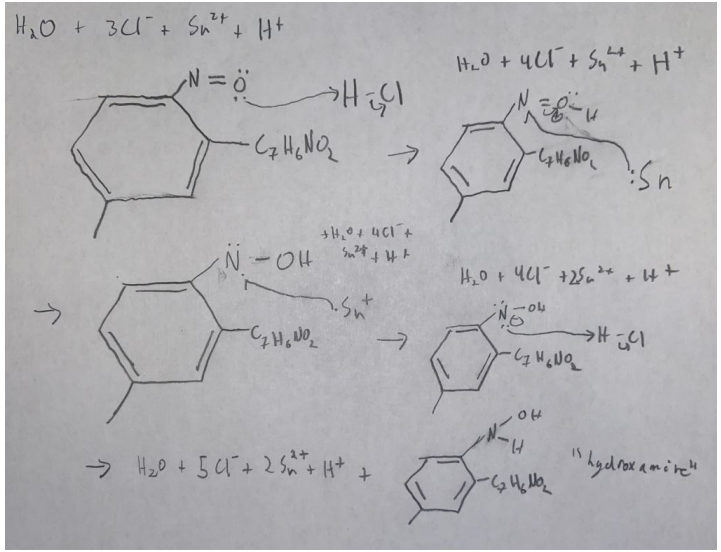


Reduction of Aromatic Nitro Groups: Mechanism #2

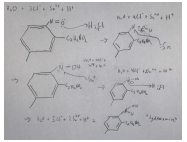


- Nitroso intermediate observed

Reduction of Aromatic Nitro Groups: Mechanism #3

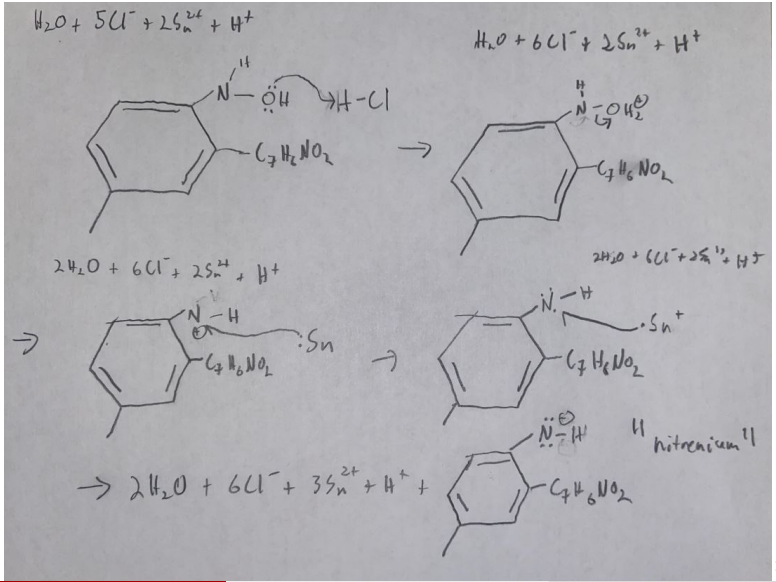


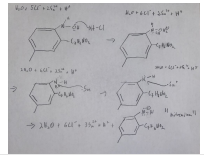
Reduction of Aromatic Nitro Groups: Mechanism #3



- Donating properties of Nitrogen make Oxygen nucleophilic
- Hydroxanamine intermediate observed

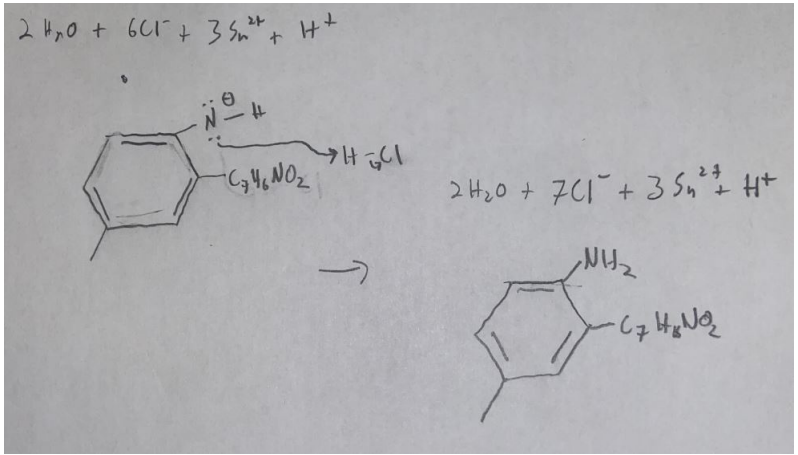
Reduction of Aromatic Nitro Groups: Mechanism #4



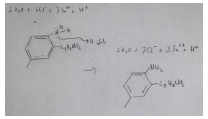


- Recall these radical attacks can happen on second go from other equivalents of Tin
- Nitrenium intermediate observed

Reduction of Aromatic Nitro Groups: Mechanism #5

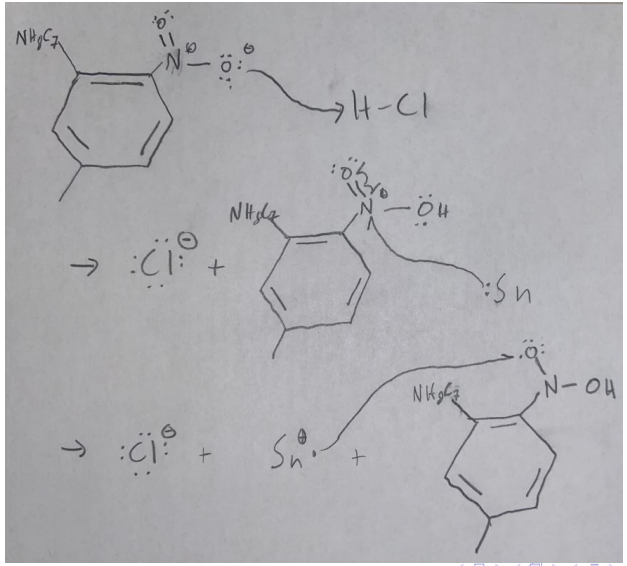


Reduction of Aromatic Nitro Groups: Mechanism #5

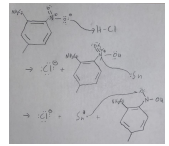


- One reduction achieved

Reduction of Aromatic Nitro Groups: Mechanism #6

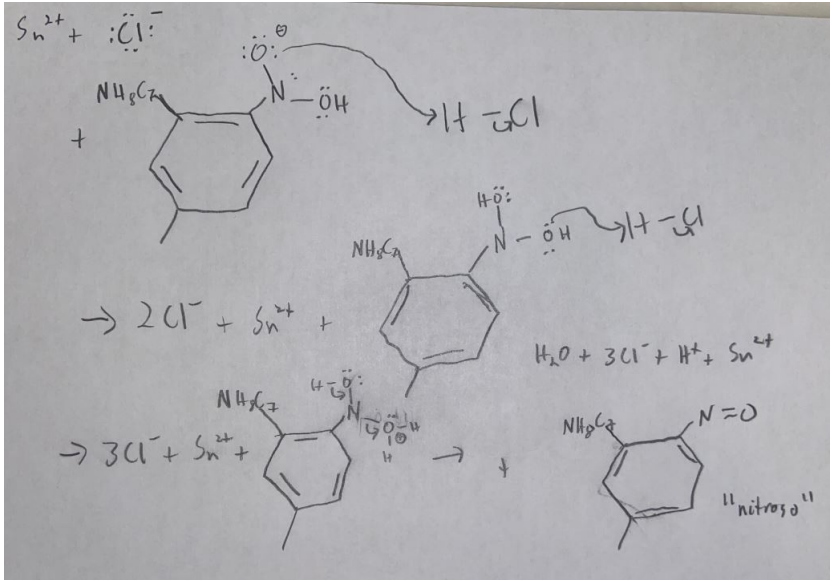


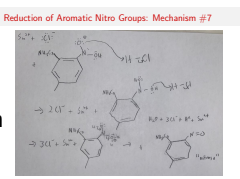
Reduction of Aromatic Nitro Groups: Mechanism #6



- The rest of this we'll zoom throught, it basically just happens twice.

Reduction of Aromatic Nitro Groups: Mechanism #7





- The rest of this we'll zoom throught, it basically just happens twice.

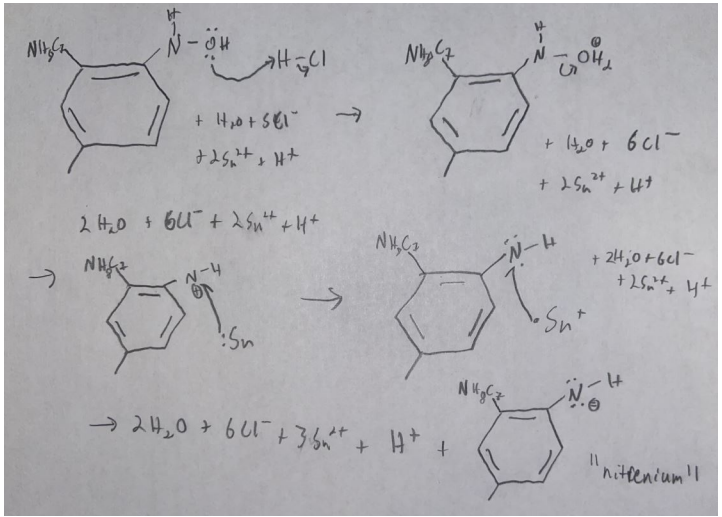
Reduction of Aromatic Nitro Groups: Mechanism #8

aromatic_nitro_reduction_eight.JP

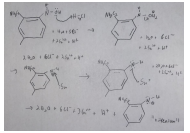
Reduction of Aromatic Nitro Groups: Mechanism #8
aromatic_nitro_reduction_eight.JP

- The rest of this we'll zoom throught, it basically just happens twice.

Reduction of Aromatic Nitro Groups: Mechanism #9

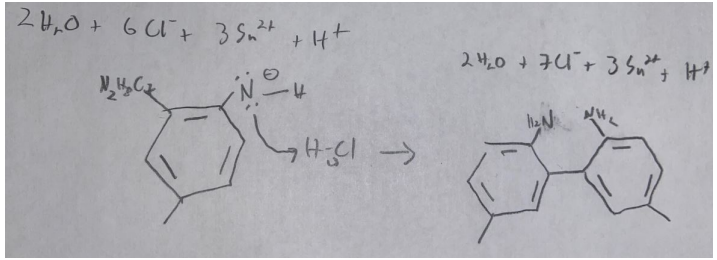


Reduction of Aromatic Nitro Groups: Mechanism #9

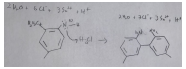


- The rest of this we'll zoom throught, it basically just happens twice.

Reduction of Aromatic Nitro Groups: Mechanism #10



Reduction of Aromatic Nitro Groups: Mechanism #10



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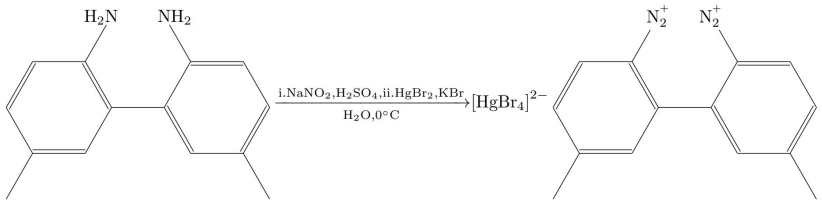
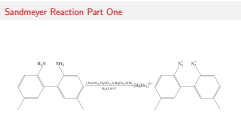
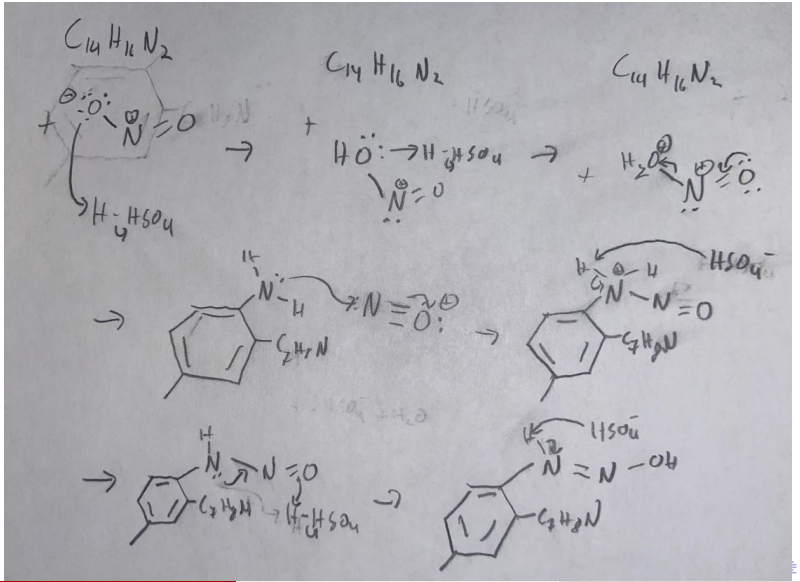
Sandmeyer Reaction Part One

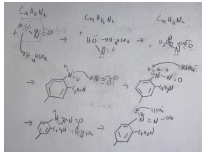




- [**Beaudoin**] is the source for both this reaction and the next one.
- It's another key SET mechanism in the second part

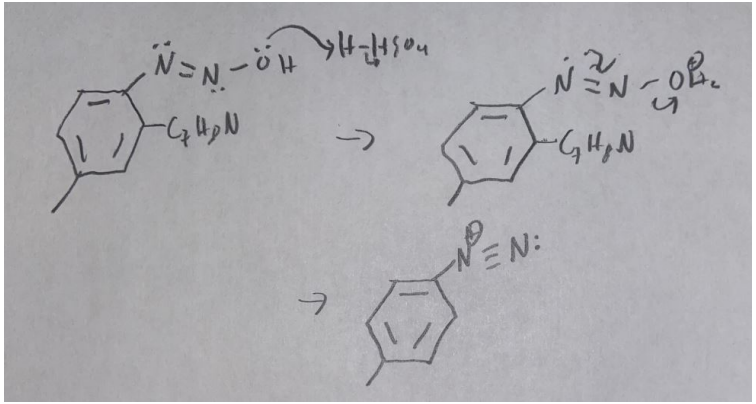
Sandmeyer Reaction Part One: Mechanism #1

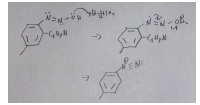




- Note HSO_4^- *asamphiproticisatplay*.

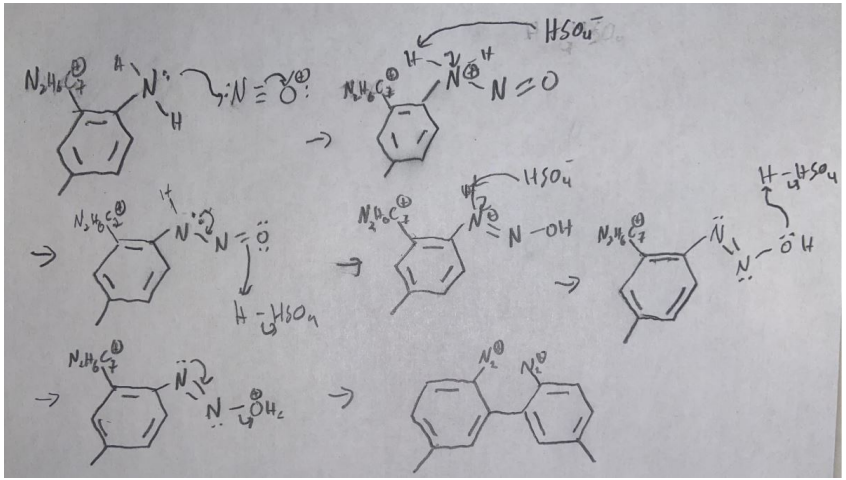
Sandmeyer Reaction Part One: Mechanism #2



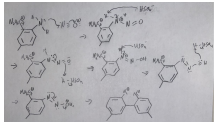


- Water production a driving force
- More substituted amino cation more stable.

Sandmeyer Reaction Part One: Mechanism #3



Sandmeyer Reaction Part One: Mechanism #3



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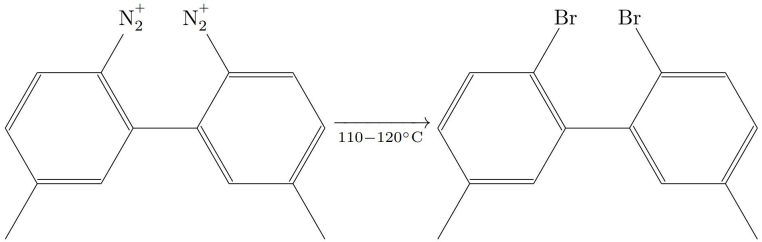
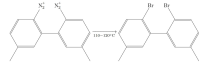
Sandmeyer Reaction Part Two

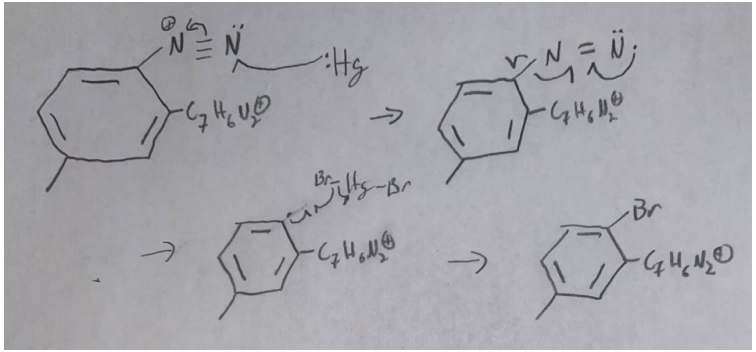


Sandmeyer Reaction Part Two

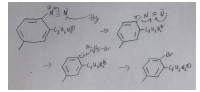


- Driving force is production of Nitrogen gas.
- I'm also going to stop copying over my paper notes here. I think I'm just kind of wasting my time.

Sandmeyer Reaction Part Two: Mechanism #1



Sandmeyer Reaction Part Two: Mechanism #1



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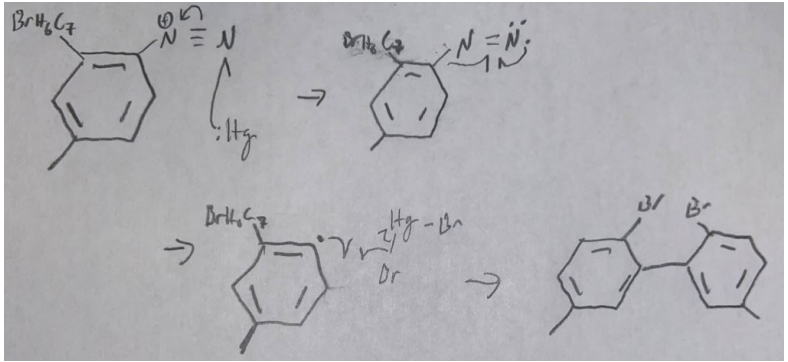
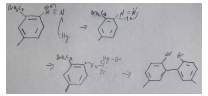
Sandmeyer Reaction Part Two: Mechanism #2



Sandmeyer Reaction Part Two: Mechanism #2



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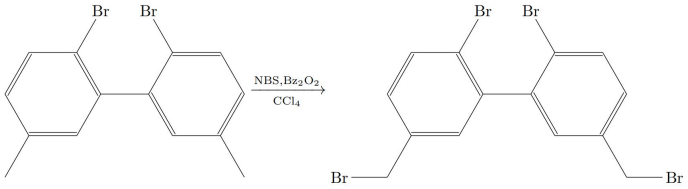
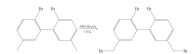
Wohl-Ziegler Reaction

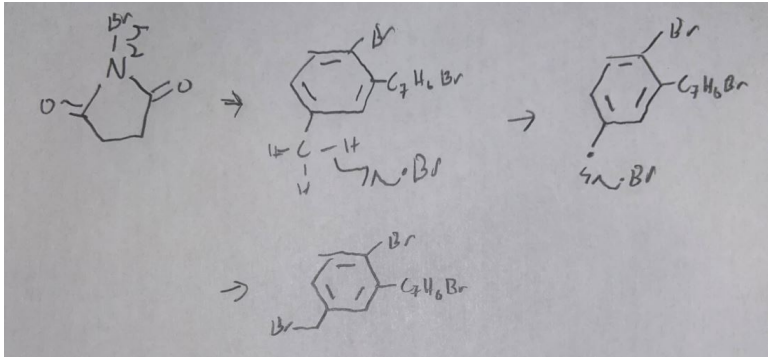


Wohl-Ziegler Reaction

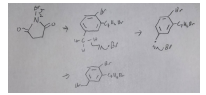


- This is the standard radical halogenation of alkanes we learned in august.

Wohl-Ziegler Reaction: Mechanism #1



Wohl-Ziegler Reaction: Mechanism #1



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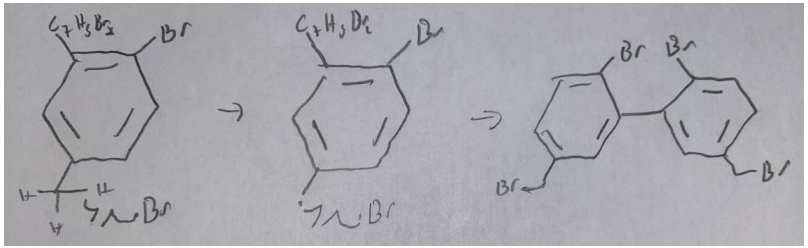
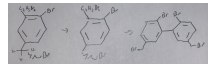
Wohl-Ziegler Reaction: Mechanism #2



Wohl-Ziegler Reaction: Mechanism #2



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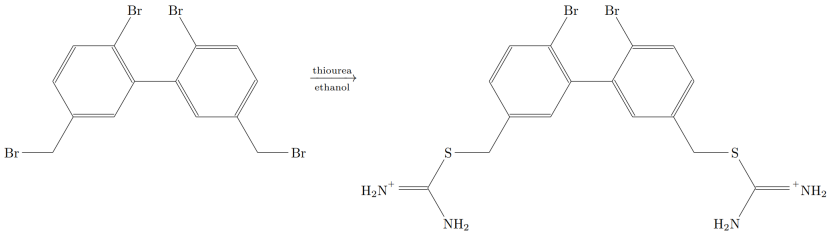
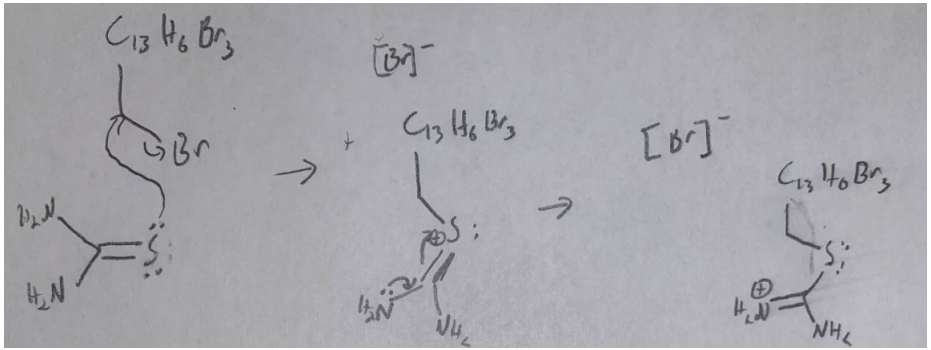
Thiolization Part One

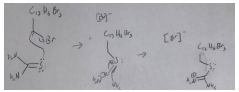


Thiolization Part One

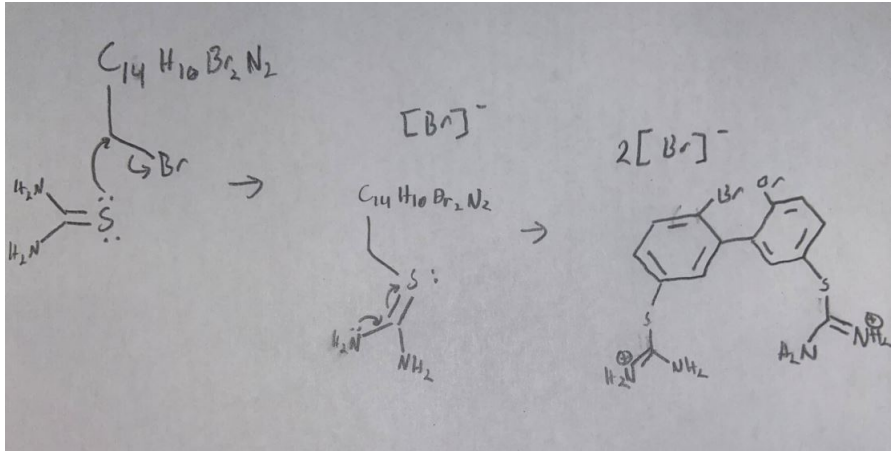
Thiolization Part One: Mechanism #1



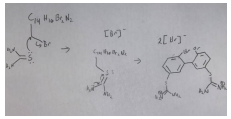
Thiolization Part One: Mechanism #1



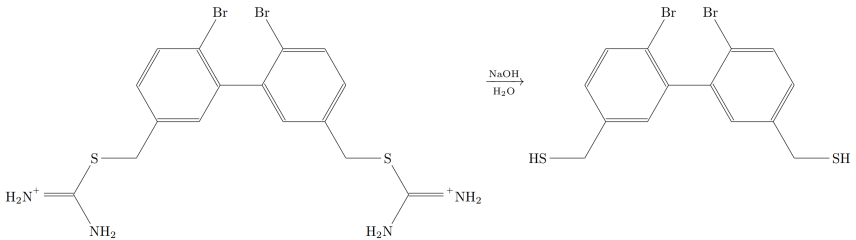
Thiolization Part One: Mechanism #2



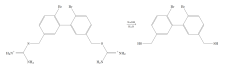
Thiolization Part One: Mechanism #2



Thiolization Part Two



Thiolization Part Two



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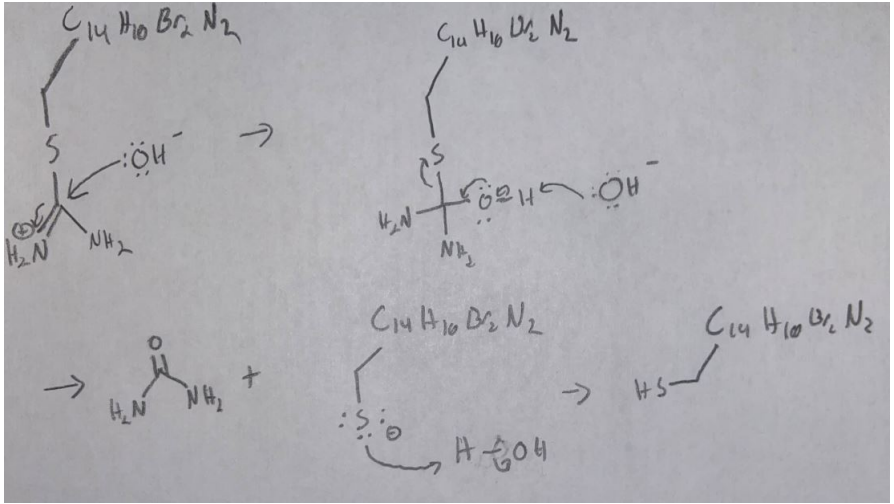

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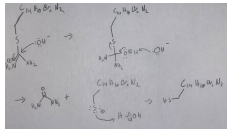

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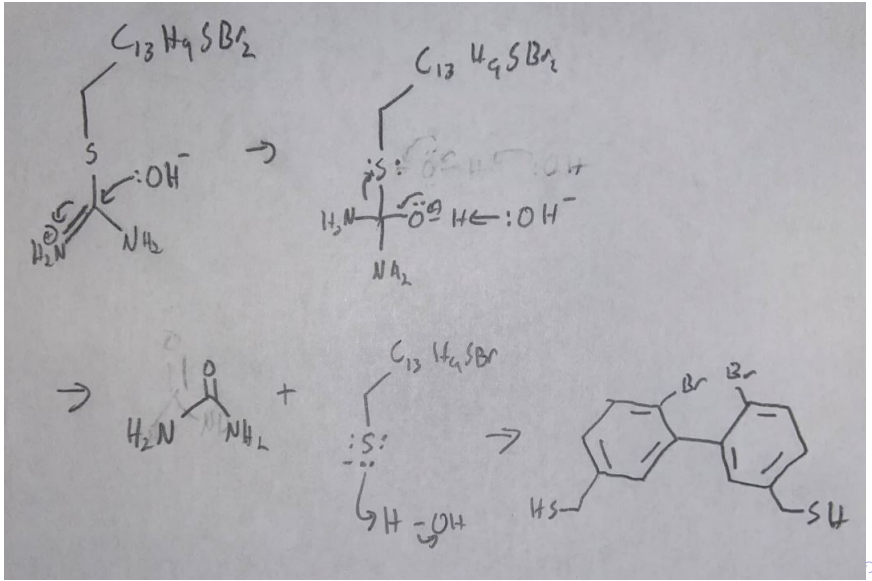

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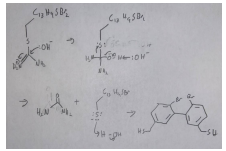
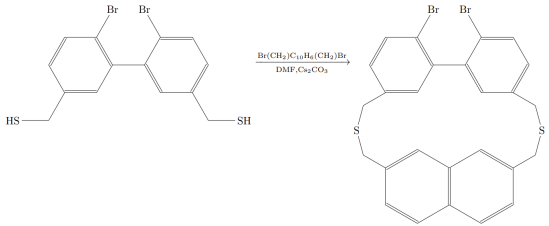
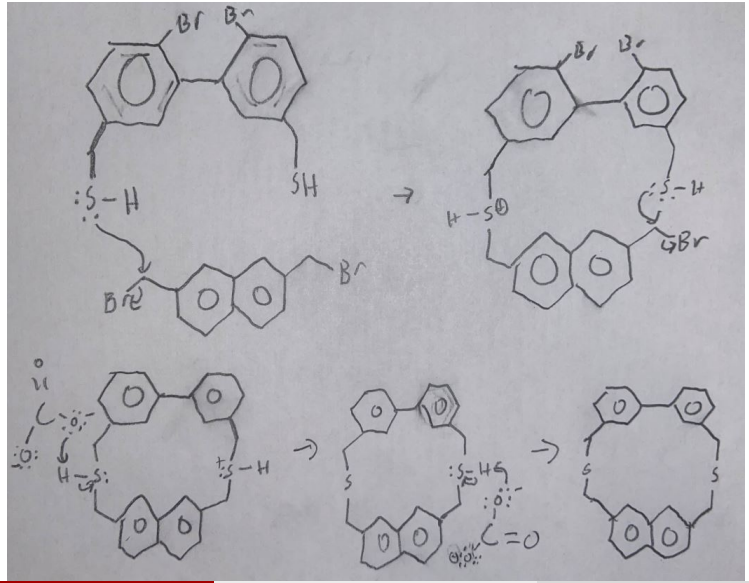


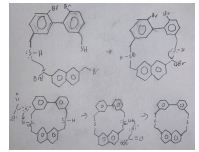
Williamson Thioether Synthesis



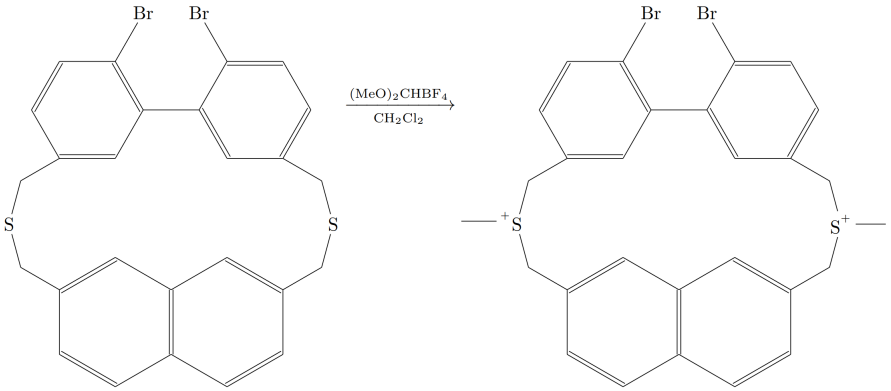
Williamson Thioether Synthesis

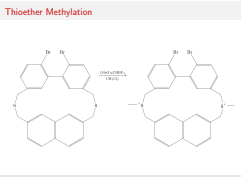
Williamson Thioether Synthesis: Mechanism #1





Thioether Methylation





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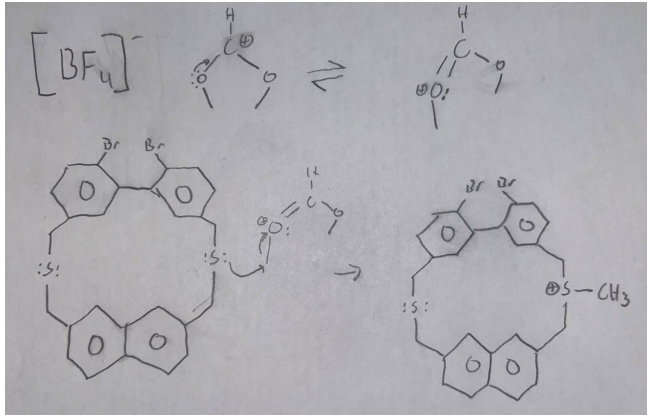

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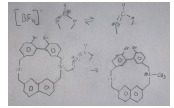

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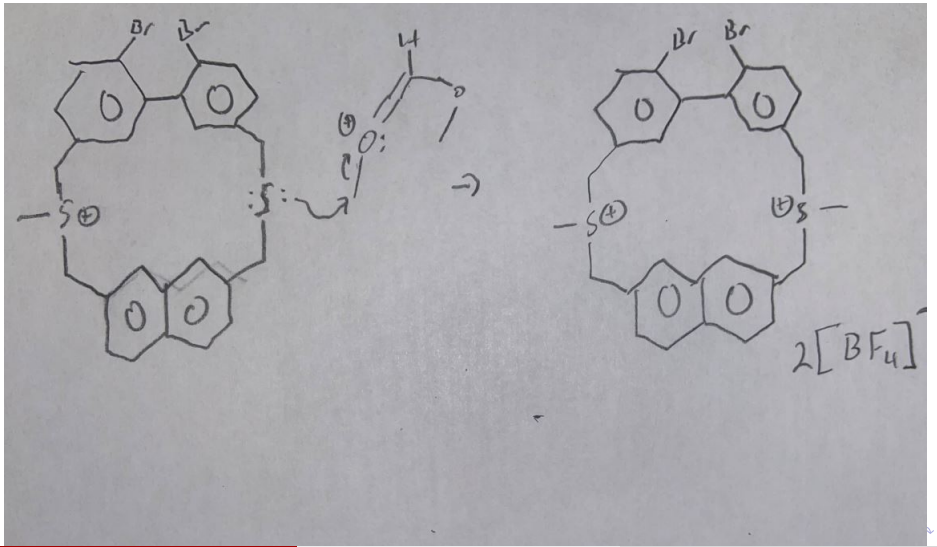

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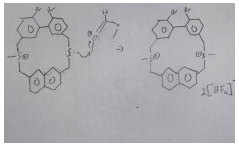
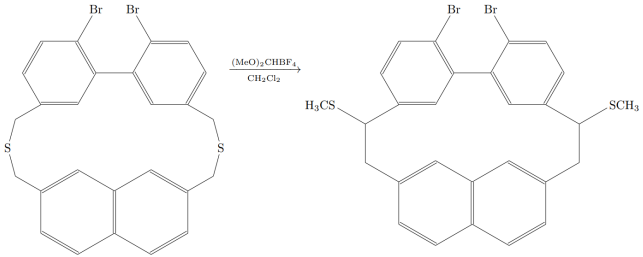


Stevens Rearrangement



Stevens Rearrangement

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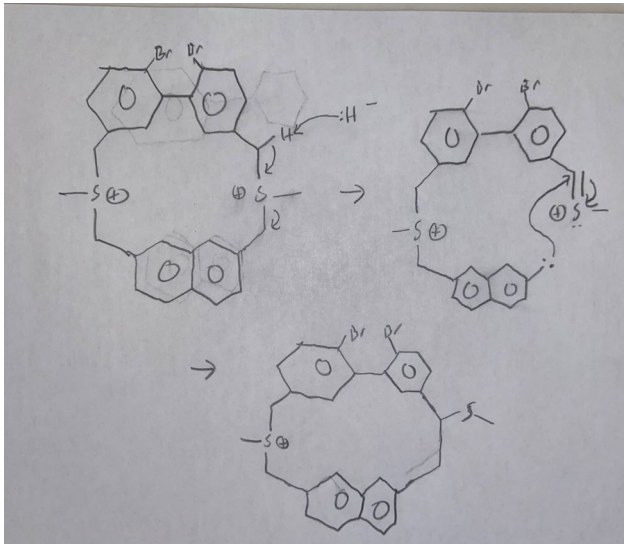

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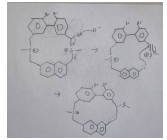

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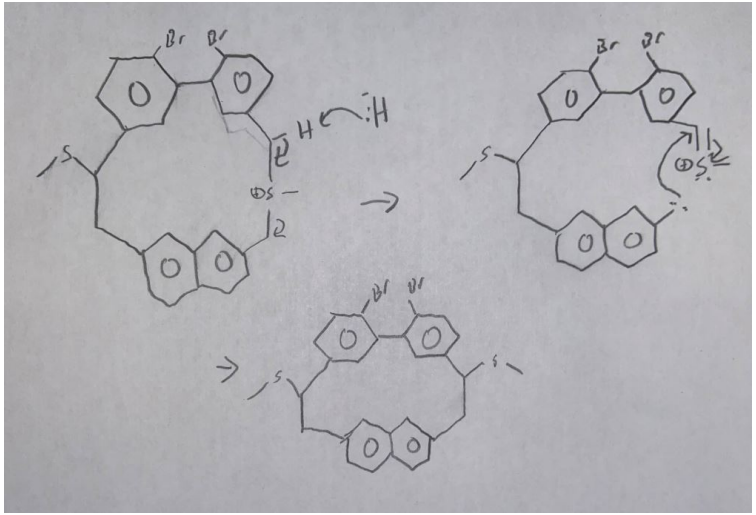

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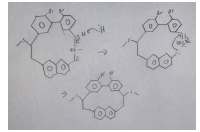
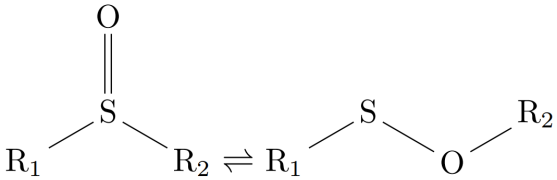


Sulfenic Ester Tautometerization



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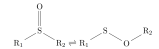

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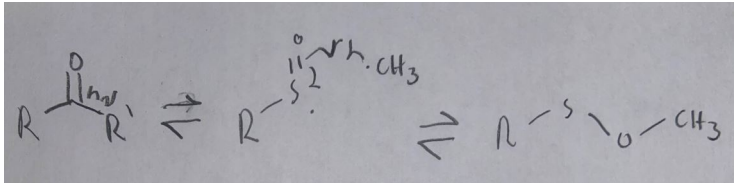

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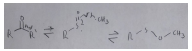
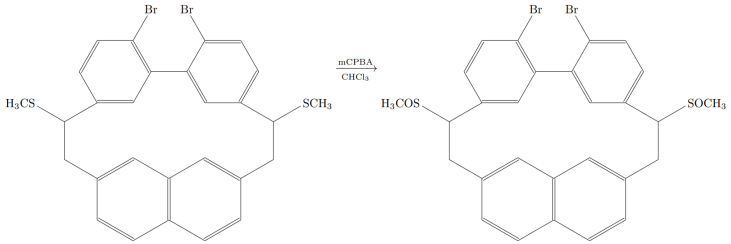
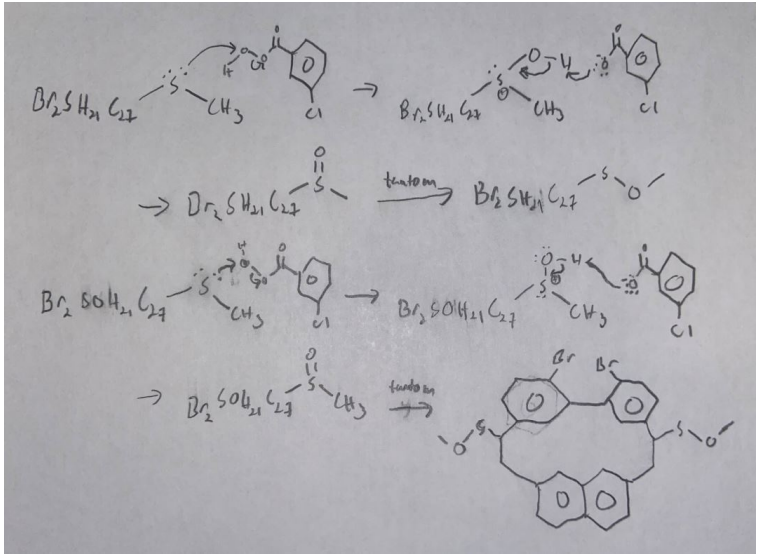


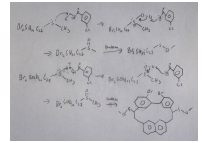
Thioether Oxidation



Thioether Oxidation

Thioether Oxidation: Mechanism #1





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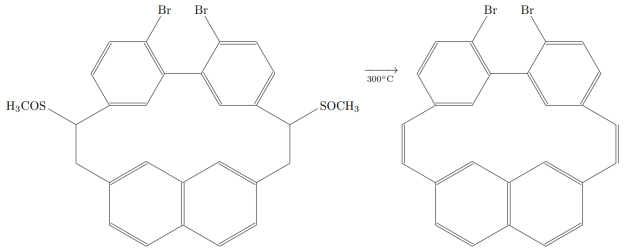
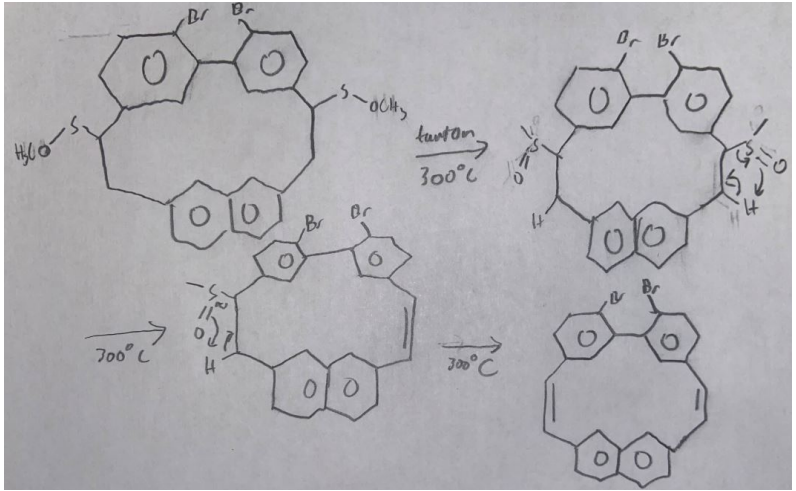
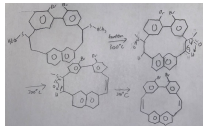


Sulfenic Ester Elimination

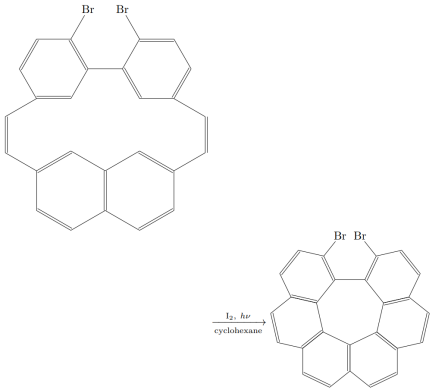
Sulfenic Ester Elimination: Mechanism #1



Sulfenic Ester Elimination: Mechanism #1



Polyaromatic Cyclization



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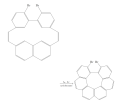

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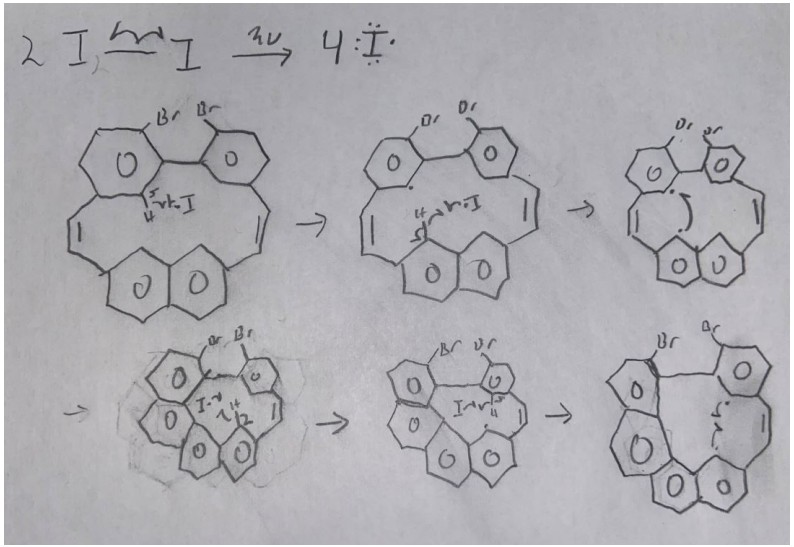
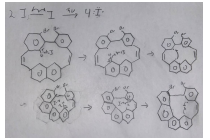
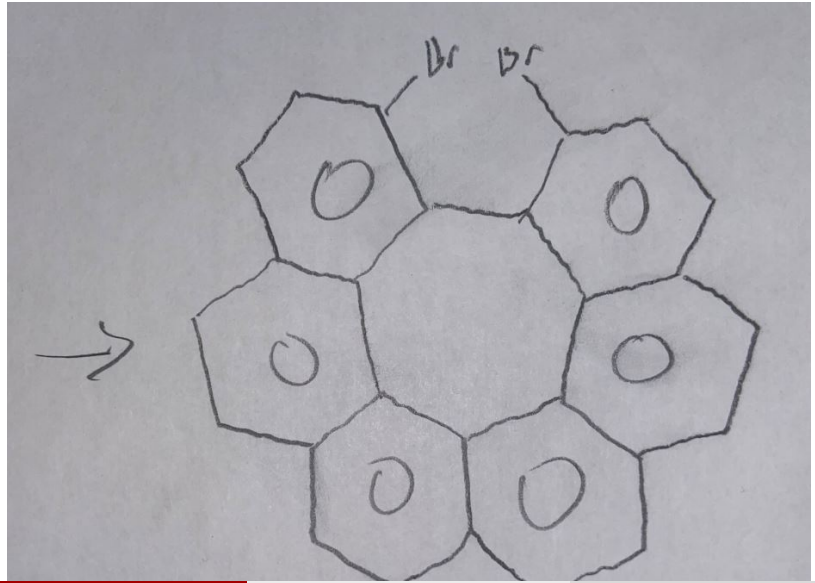


Polyaromatic Cyclization: Mechanism #1



Polyaromatic Cyclization: Mechanism #2



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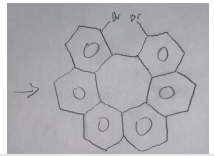
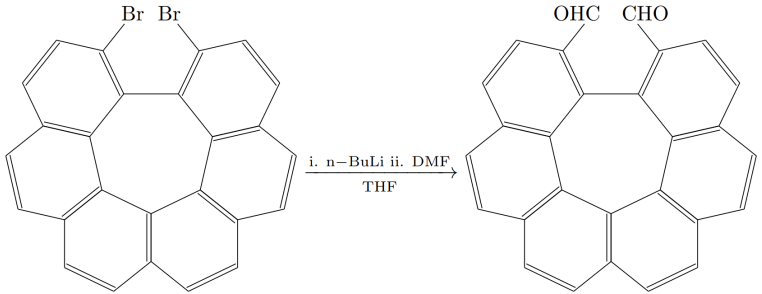
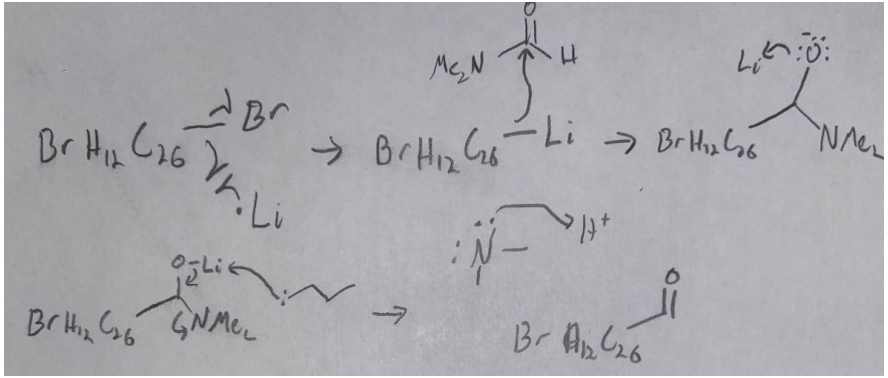


Bouveault Aldehyde Synthesis

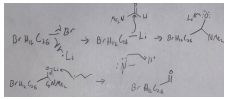


Bouveault Aldehyde Synthesis

Bouveault Aldehyde Synthesis: Mechanism #1



Bouveault Aldehyde Synthesis: Mechanism #1



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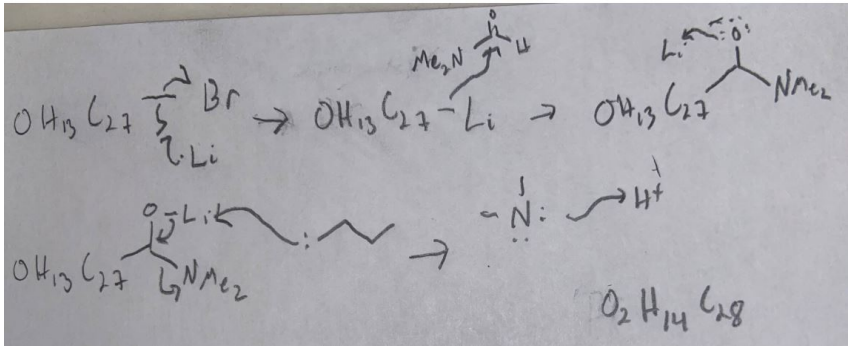

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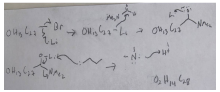
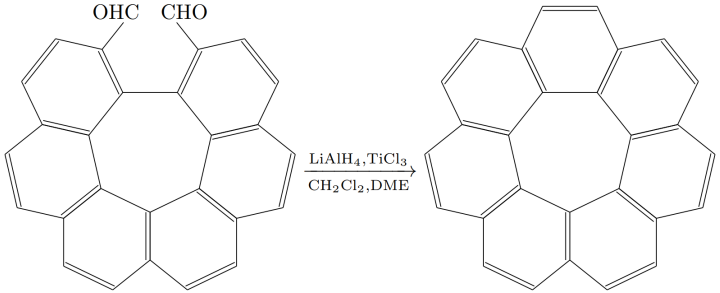


McMurry Reaction



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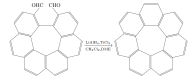
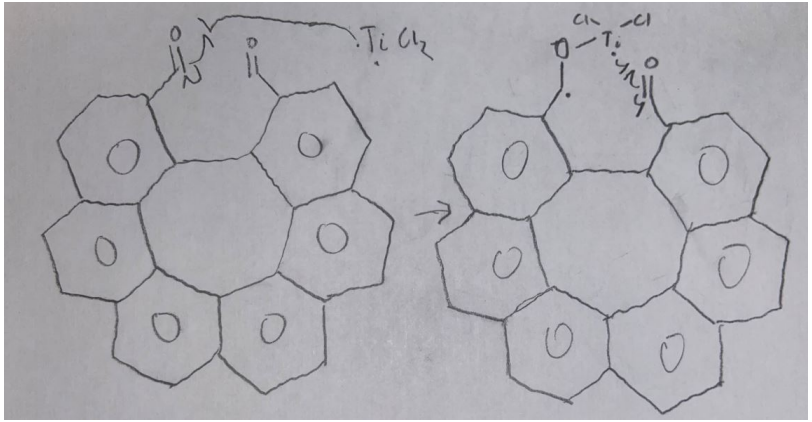


McMurry Reaction: Mechanism #1



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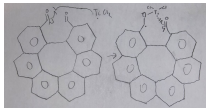

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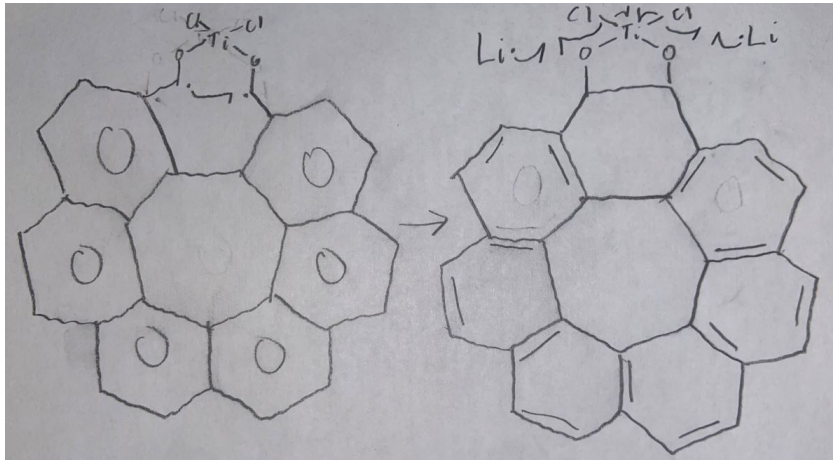

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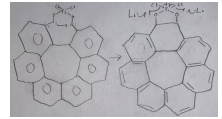

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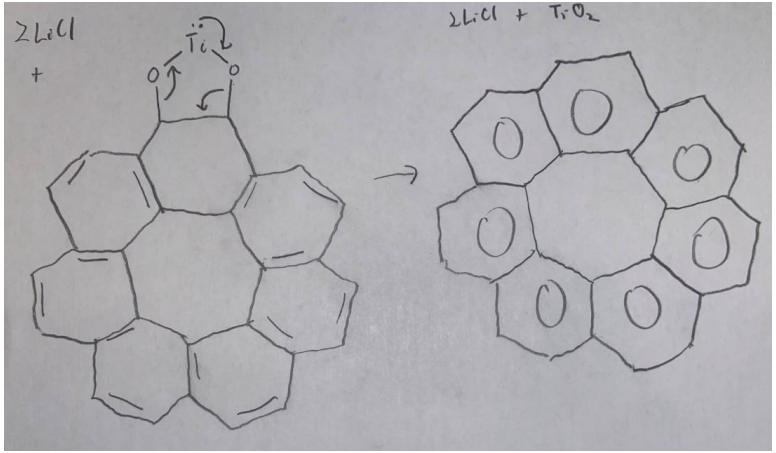
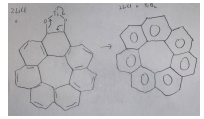


McMurry Reaction: Mechanism #3



References

- Koji, Yamamoto; Tadashi, Harada; Yoshio, Okamoto; Hiroaki, Chikamatsu; Masao, Nakazaki; Yasushi, Kai; Takuo, Nakao; Mitsuya, Tanaka; Shigeharu, Harada; Nobutami, Kasai (1988). "Synthesis and molecular structure of [7]circulene". *Journal of the American Chemical Society*. 110 (11): 3578–3584. doi:10.1021/ja00219a036
- F. Ullmann; Jean Bielecki (1901). "Ueber Synthesen in der Biphenylreihe". *Chemische Berichte*. 34 (2): 2174–2185. doi:10.1002/cber.190103402141
- Smith, Michael B.; March, Jerry (2007), *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* (6th ed.), New York: Wiley-Interscience, ISBN 978-0-471-72091-1
- "Global Graphene Market Size is Expected to Reach 151.4 Million and Register a CAGR of 47.7 percent by 2021, Market Trends, Growth and Forecast - Valuates Report". PR Newswire. Cision. 25 November 2019. Retrieved 29 January 2020.

References

- Koji, Yamamoto; Tadashi, Harada; Yoshio, Okamoto; Hiroaki, Chikamatsu; Masao, Nakazaki; Yasushi, Kai; Takuo, Nakao; Mitsuya, Tanaka; Shigeharu, Harada; Nobutami, Kasai (1988). "Synthesis and molecular structure of [7]circulene". *Journal of the American Chemical Society*. 110 (11): 3578–3584. doi:10.1021/ja00219a036
- F. Ullmann; Jean Bielecki (1901). "Ueber Synthesen in der Biphenylreihe". *Chemische Berichte*. 34 (2): 2174–2185. doi:10.1002/cber.190103402141
- Smith, Michael B.; March, Jerry (2007), *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure* (6th ed.), New York: Wiley-Interscience, ISBN 978-0-471-72091-1
- "Global Graphene Market Size is Expected to Reach 151.4 Million and Register a CAGR of 47.7 percent by 2021, Market Trends, Growth and Forecast - Valuates Report". PR Newswire. Cision. 25 November 2019. Retrieved 29 January 2020.

References

- *Synarchive*. Beaudoin, Daniel. "Synthesis of [7]Circulene". 2011.
- Karadakov, Peter B. (February 2016). "Do large polycyclic aromatic hydrocarbons and graphene bend? How popular theoretical methods complicate finding the answer to this question" (PDF). *Chemical Physics Letters*. 646: 190–196. doi:10.1016/j.cplett.2015.12.068.
- David R. Lide (ed), *CRC Handbook of Chemistry and Physics*, 84th Edition. CRC Press. Boca Raton, Florida, 2003; Section 10, Atomic, Molecular, and Optical Physics; Ionization Potentials of Atoms and Atomic Ions
- http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/2/vlu/oxidation,e

References

- Synarchive. Beaudoin, Daniel. "Synthesis of [7]Circulene". 2011.
- Karadakov, Peter B. (February 2016). "Do large polycyclic aromatic hydrocarbons and graphene bend? How popular theoretical methods complicate finding the answer to this question" (PDF). Chemical Physics Letters. 646: 190–196. doi:10.1016/j.cplett.2015.12.068.
- David R. Lide (ed), CRC Handbook of Chemistry and Physics, 84th Edition. CRC Press. Boca Raton, Florida, 2003; Section 10, Atomic, Molecular, and Optical Physics; Ionization Potentials of Atoms and Atomic Ions
- http://www.chemgapedia.de/vsengine/vlu/vsc/en/ch/2/vlu/oxidation,e

References

- https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map3A_Orga
- *Name Reactions*: A Collection of Detailed Reaction Mechanisms By Jie Jack Li
- https://sci-hub.tw/https://pubs.acs.org/doi/10.1021/jo0160625

References
https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map3A_Orga
Name Reactions: A Collection of Detailed Reaction Mechanisms By Jie Jack Li
https://sci-hub.tw/https://pubs.acs.org/doi/10.1021/jo0160625