## Permission Slip for Lab Change

*Winter 2020*

Once you have been assigned a permanent lab section, if you need to change ONE session date, please print and bring this form to the lab the day you attend the make-up session for the lab. Complete the upper portion and ask Dr. Rashmi, Dr. Pell or Dr. Peneau to sign the form and assign you a spot in the lab. Ask the TA to whom you have been assigned to complete the centre portion of the form and to return the form to you. Attach the form to the front of your lab report when you submit it. If you have documentation, you will have one week from the day you perform the experiment to submit your report. If you do not have documentation, you must submit the report at your normal submission date and time.

**Student Requesting Section Change:** Orpita Das

**Student Number:** 300112387

**Reason for change:** missed lab

**Document provided:** YES (NO)

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**Normal Lab Section:** Tuesday Wednesday (Thursday)

(Morning) Afternoon

(Odd Week) Even Week

(please circle ONE choice from EACH line above)

**Regular TA's Name**: Atousa Khanzadeh

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**Replacement Lab Section:** Tuesday Wednesday (Thursday)

Morning (Afternoon)

(Odd Week) Even Week

(please circle ONE choice from EACH line above)

**Replacement TA's Name:** Weiyi Zhou

**Replacement TA's Signature:** Weiyi Zhou

**Date:** 2020.3.5

**TA Evaluation for the lab session:** 10 /10

**(attach this sheet to the report when it is handed in or the report will not be graded)**

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**Signed by Dr. Rashmi/Dr. Pell/Dr. Peneau/Mr. Goudreault:** [signature] Dr. Terry

# Experiment 4:
# Stereochemical Analysis of the Reduction of Benzel

Orpita Das - 300112387

Regular TA: Atousa Khanzadeh
TA for this lab: Weiyi Zhou

Date performed: March 5th, 2020
Date due: March 12th, 2020

## Introduction

Oxidation-reduction (aka redox) reactions are chemical reactions that involve transferring electrons. In such reactions, the compound undergoing electron loss is oxidized, while the compound that subsequently gains electrons is reduced. In organic reactions, redox reactions are defined relative to the bonds formed or broken from carbon: oxidation means making more bonds to atoms that are more electronegative than carbon, and reduction means making more bonds to atoms that are less electronegative than carbon. Typically, the more electronegative atom is oxygen whereas the less electronegative atom is hydrogen. In this experiment, we will perform a redox reaction between sodium borohydride ($NaBH_4$) and benzil with the goal of reducing the carbonyl groups of benzil. Various laboratory techniques will be carried out for this experiment, including thin layer chromatography (TLC), recrystallization, and suction filtration.

Benzil contains two carbonyl groups, and thus undergoes reduction twice. Since the nucleophile will attack each carbonyl one at a time [1], partially reduced benzil (benzoin) will be present in the mixture as the reaction progresses. TLC, which involves separating mixtures based on electronegativity, will be used to separate the partially and fully reduced benzil products to determine if it has reached completion.

Recrystallization is used as a purification technique and relies on solubility. The goal of recrystallization is to crystallize the product with as few impurities as possible in order to isolate the preferred fully-reduced product, hydrobenzoin.

## Procedure

As outlined in the lab manual ("Experiment 4: Stereochemical Analysis of the Reduction of Benzil", Organic Chemistry Laboratory Manual, Department of Chemistry, University of Ottawa, 2019, Exp. 4, pg. 7).

## Observations

Benzil

- yellow, granulated crystalline solids

Dichloromethane (DCM)

- transparent & colourless liquid

Ethanol

- transparent & colourless liquid

$NaBH_4$

- white, granulated crystalline solids

Solution of benzil + DCM + ethanol

- yellow, translucent solution

Solution of benzil + DCM + ethanol + $NaBH_4$
- loss of yellow colour
- transparent & colourless solution

## Table of Reagents

**Table 1.** Table of all reagents used in this experiment.

| Compound | Mol. Wt. (g/mol) | Amount | Density (g/mL) | mmol |
|---|---|---|---|---|
| Benzil | 210.23 [4] | 1.10 g | | 5.232 |
| $NaBH_4$ | 37.83 [3] | 0.3 g | | 7.912 |
| Ethanol | 46.07 [5] | 5 mL | 0.790 [5] | |
| $CH_2Cl_2$ | 84.93 [6] | 5 mL | 1.326 [6] | |

## Results

**Figure 1.** TLC analysis obtained after reaction mixture reached room temperature (TLC Plate 1) and final product after recrystallization (TLC Plate 2).

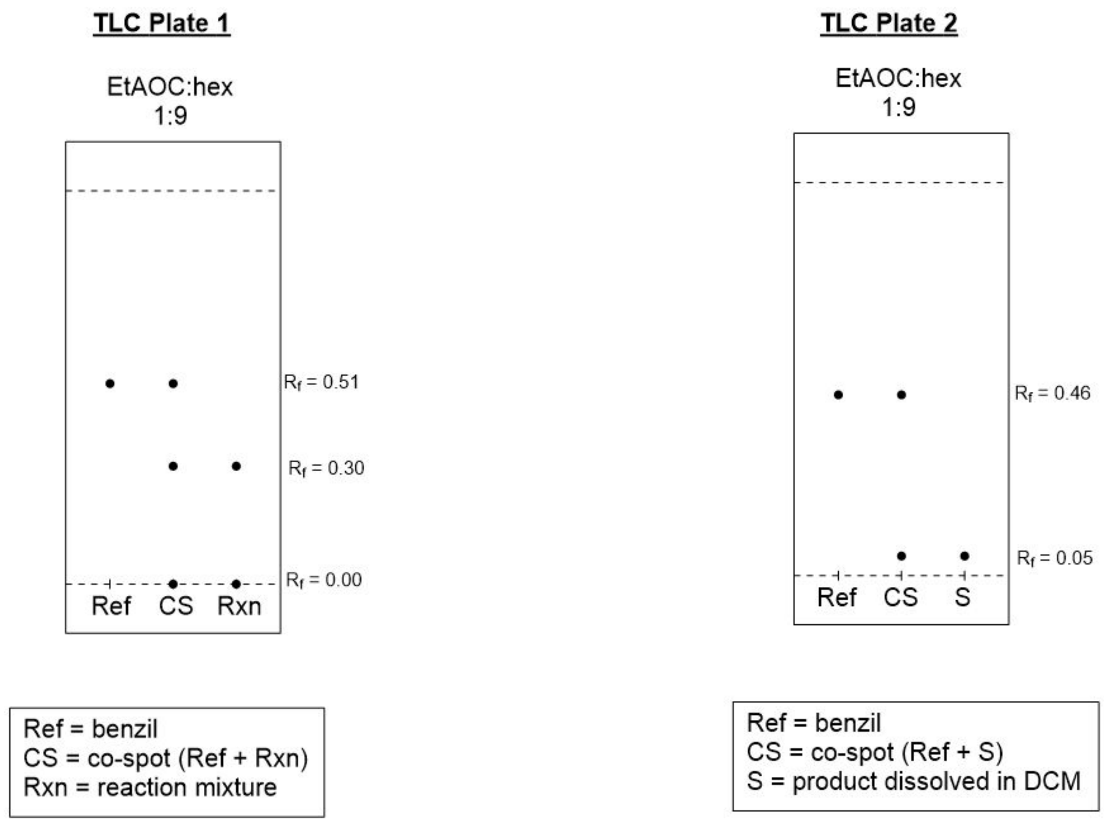



**Table 2.** Table of results obtained for the final product (obtained after recrystallization).

| Compound | Mol. Wt. (g/mol) | Amount | mmol | Percent yield |
|---|---|---|---|---|
| Hydrobenzoin | 214.26 g/mol | 1.5 g | 7.0 | 104 % |

**Figure 2.** Reaction mechanism of the reduction of benzil by sodium borohydride in a solution of ethanol and dichloromethane.

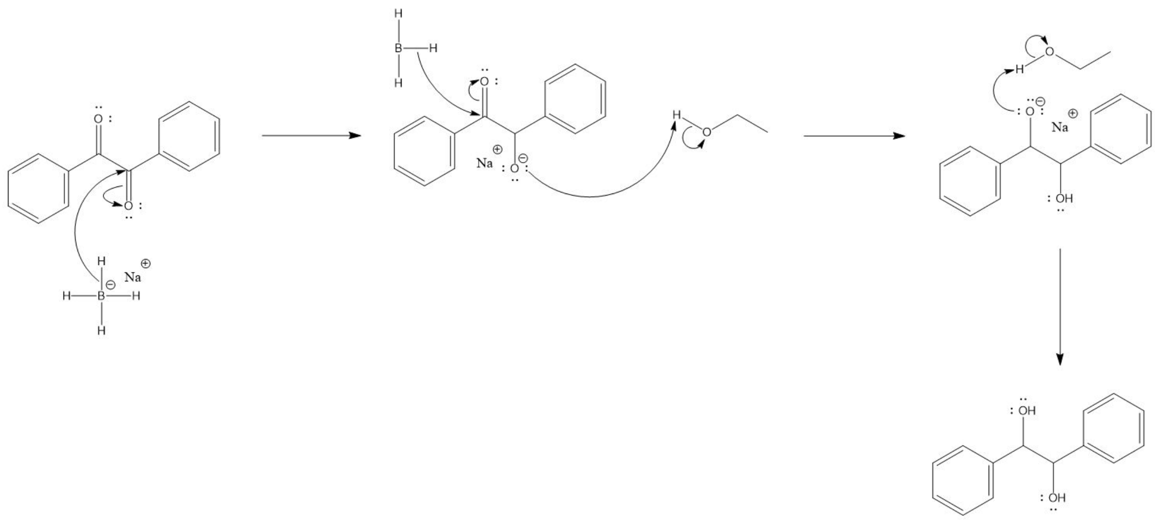
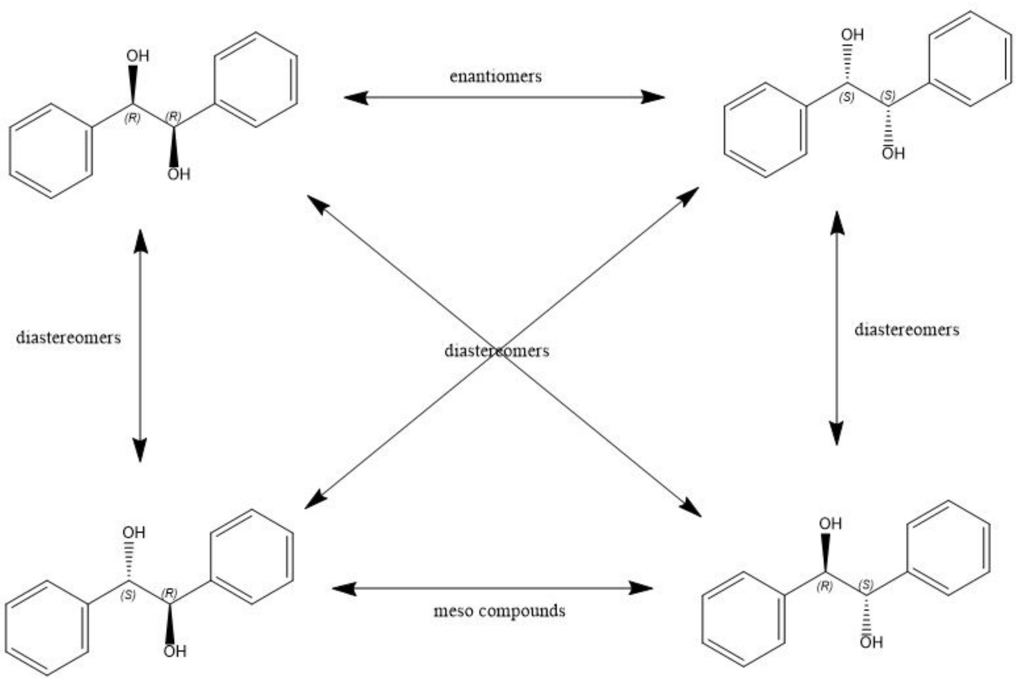



**Figure 3.** Full stereochemical analysis of hydrobenzoin.




# Calculations

Percent Yield

% yield = (amount obtained (g) / theoretical amount possible (g)) x 100%
= (1.05 g / 1.01 g) x 100 %
= 104 %

Sample $R_f$ Value: TLC Plate 1 **(Figure 1)**, Ref lane

$R_f$ = distance travelled/total distance
= 2.4 cm/4.7 cm
= 0.51

## Discussion

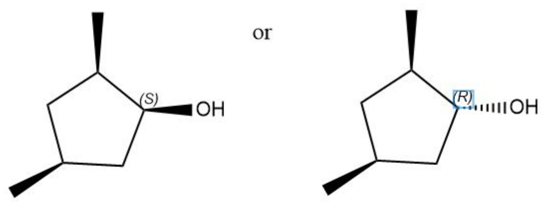
- the goal of this lab was to reduce the carbonyl groups of benzil using sodium borohydride
- TLC Plate 1 (Figure 1) was performed to verify if our redox reaction had reached completion
    - Rxn lane has two spots, indicating two compounds present
    - large difference between $R_f$ values of each spot indicates high difference in polarity
    - presence of two compounds may be due to reduction of only 1 carbonyl group of some of the benzil, resulting in production of benzoin
        - hydride nucleophile attacks 1 carbonyl at a time
        - indicates reaction did not reach completion, both carbonyl groups of all the benzil were not reduced
    - eluant is highly nonpolar, therefore spot w/ higher $R_f$ is more nonpolar
    - spot w/ lower $R_f$ is more polar, more attracted to stationary phase, which is also highly polar silica gel
        - slower spot is most like the fully reduced compound, hydrobenzoin
        - has greater number of dipole moments than benzoin due to presence of 2 alcohol groups, has a greater overall polarity
        - capable of forming hydrogen bonds and dipole-dipole bonds
        - benzoin only has one alcohol group, has 1 less dipole moment than hydrobenzoin
        - closer to the reference spot, therefore has to more closely resemble benzil
        - both share at least one carbonyl, therefore faster one in rxn lane most likely benzoin
    - impure/incomplete reaction is most likely due to the reaction occurring in an ice bath and then waiting for it to reach room temperature
        - lack of thermal energy impedes reaction rate

        - solutes dissolve best at temperatures close to their boiling point, benzil dissolves best in ethanol at high temps [2]
        - indicates we did not wait long enough for the solution to reach room temperature, should have waited longer and used a thermometer instead of relying solely on approximations in the lab manual and using our fingers to feel how cold the flask was
- in order to obtain just the desired product (the completely reduced benzil: hydrobenzoin), we need to use a purification method
- recrystallization & subsequently suction filtration was used to dissolve the impurities and obtain the desired product
    - recrystallization takes advantage of the fact that different substances have varying solubilities at different temperatures
    - since hydrobenzoin is a polar compound, a polar solvent was used (hot water)
    - water has a higher melting point than DCM & ethanol, therefore it precipitated out first, allowing us to filter out the crystals via suction filtration
    - percent yield was > 100 %, indicating an error occurred
        - most likely due to the fact that suction filtration is not an effective way to dry the crystals
        - time constraints of the lab did not allow us to fully dry the crystals, it was still a bit damp when we had to weigh it
        - most likely not due to presence of impurities in final product, as TLC plate 2 (Figure 1) demonstrates only 1 highly-polar compound in the sample lane
- benzoin has 2 stereoisomers & hydrobenzoin has 3 stereoisomers
    - initial reduction of benzil has equal chance of top or bottom face nucleophilic attack, therefore equal chance of either of the 2 stereoisomers of benzoin to be present in the mixture
        - racemic mixture
    - following reduction was done by ethanol, as it is a polar protic solvent and therefore readily reduces the negatively charged oxygen instead of $NaBH_4$ (comparatively weak nucleophile) [7], forcing sodium borohydride to attack from the face that is furthest away from the resulting alcohol group
        - R,S & S,R (anti) stereoisomers have less distance b/w alcohol groups
            - repulsion of like charges occupying limited space creates competition for space simultaneously with repulsive force, creates steric strain, energetically not favourable, therefore needs to create greater distance
        - therefore major product has greatest distance b/w the resulting alcohol groups: R,R & S,S (syn) stereoisomers are most favourable

## **Questions**

1. true
    - when boiling point of the solvent is higher than the melting point of the compound, the compound forms the liquid phase first when heating up the solution
    - in the liquid phase, the impurities are more miscible with the compound, thus as you cool the solution, the impurities disrupt the formation of a crystal lattice
    - this prevents proper crystal formation, and results in the compound precipitating in the liquid form, which is referred to as “oiling out”
2. heated first then cooled
    - max yield = mass soluble at higher temp - mass soluble at lower temp
      = 39. 1 g - 35.6 g
      max yield = 3.5 g
3.
    - successful recrystallization involves heating a mixture to the boiling point of a solvent that has high affinity for the impurities in the mixture in order to dissolve them
    - the boiling point of methanol is 65 °C [2], the student did not heat the mixture enough to dissolve the impurities -- it would be improved if the student could heat the solution to the boiling point
    - methanol is not as efficient as a solvent, as solvents that have high solubilities at high temperatures and low solubilities at low temperatures crystallize better, thus changing the solvent may improve the yield
    - using only a polar solvent for recrystallization of the crude product may cause all the compounds to dissolve in the solvent, as there is no other solvent to compete for affinities, thus adding a nonpolar solvent would allow for better purification
4. a.
    - carboxylic acid is a strong bronsted acid, therefore it is polar & protic
    - acid-base reactions occur more readily than nucleophilic addition
    - $NaBH_4$ is a weak nucleophile, therefore it cannot attack the carbonyl as it is not strong enough to reduce the acid - carboxylic acid is a proton donor and thus does not readily participate in nucleophilic addition with a weak nucleophile

   b.
    - carboxylic acid instead donates its proton to the hydride to form hydrogen gas (the bubbles) and butanoate (conjugate base of butanoic acid)
5.

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- since there is steric hindrance in the front face of the compound, the nucleophilic attack from DIBAL occurs from the back face (facing away from the methyl groups) as it is energetically favourable

## References

1. “Experiment 4: Stereochemical Analysis of the Reduction of Benzil”, Organic Chemistry Laboratory Manual, Department of Chemistry, University of Ottawa, 2019, Exp. 4, pg. 4
2. “Experiment 4: Stereochemical Analysis of the Reduction of Benzil”, Organic Chemistry Laboratory Manual, Department of Chemistry, University of Ottawa, 2019, Exp. 4, pg. 6
3. National Center for Biotechnology Information. PubChem Database. Sodium borohydride, CID=4311764, https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-borohydride (accessed on Mar. 12, 2020)
4. National Center for Biotechnology Information. PubChem Database. Benzil, CID=8651, https://pubchem.ncbi.nlm.nih.gov/compound/Benzil (accessed on Mar. 12, 2020)
5. National Center for Biotechnology Information. PubChem Database. Ethanol, CID=702, https://pubchem.ncbi.nlm.nih.gov/compound/Ethanol (accessed on Mar. 12, 2020)
6. National Center for Biotechnology Information. PubChem Database. Dichloromethane, CID=6344, https://pubchem.ncbi.nlm.nih.gov/compound/Dichloromethane (accessed on Mar. 12, 2020)
7. “Experiment 4: Stereochemical Analysis of the Reduction of Benzil”, Organic Chemistry Laboratory Manual, Department of Chemistry, University of Ottawa, 2019, Exp. 4, pg. 3

## Raw Data

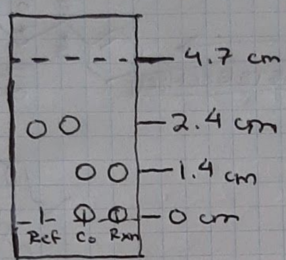
Experiment 4

Part A

1.1 g benzil
↳ yellow, powdery substance
↳ loss of colour after addition of $NaBH_4$
↳ added 15 mL hot water instead of 10 mL
↳ added 15 mL hot water instead of 20 mL
→ mass obtained = 1.5 g

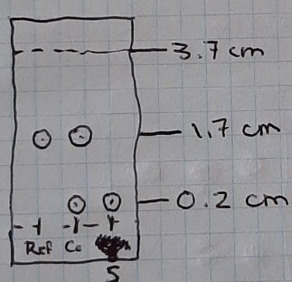
TLC Plates

①




Ref : benzil
Co-spot = benzil + rxn
Rxn : reaction mixture

②




Ref : benzil
Co-spot ;
S : product dissolved in DCM

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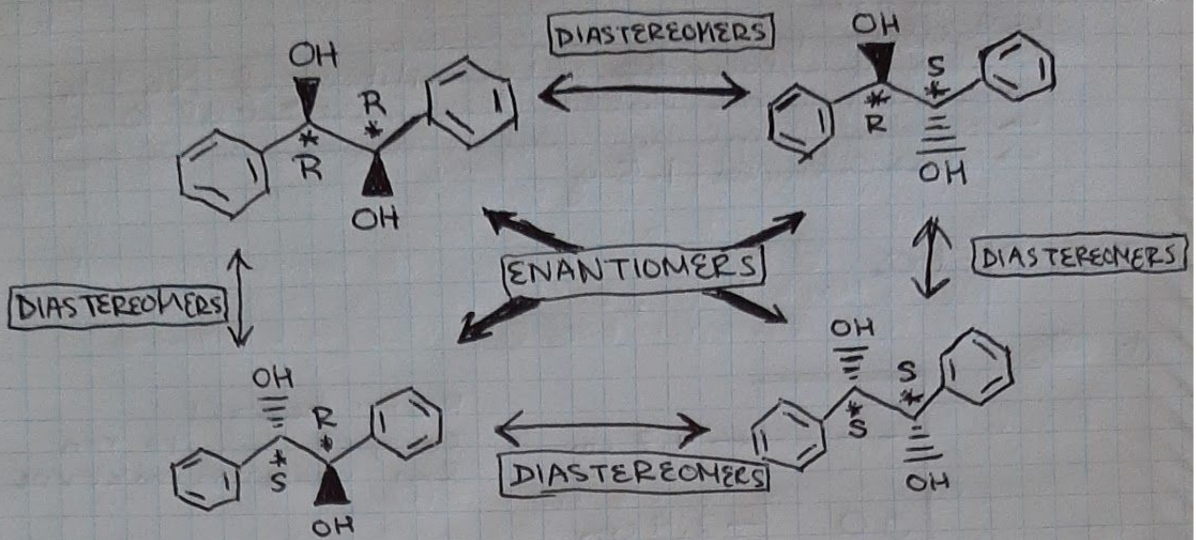
# Experiment 4

## Part B

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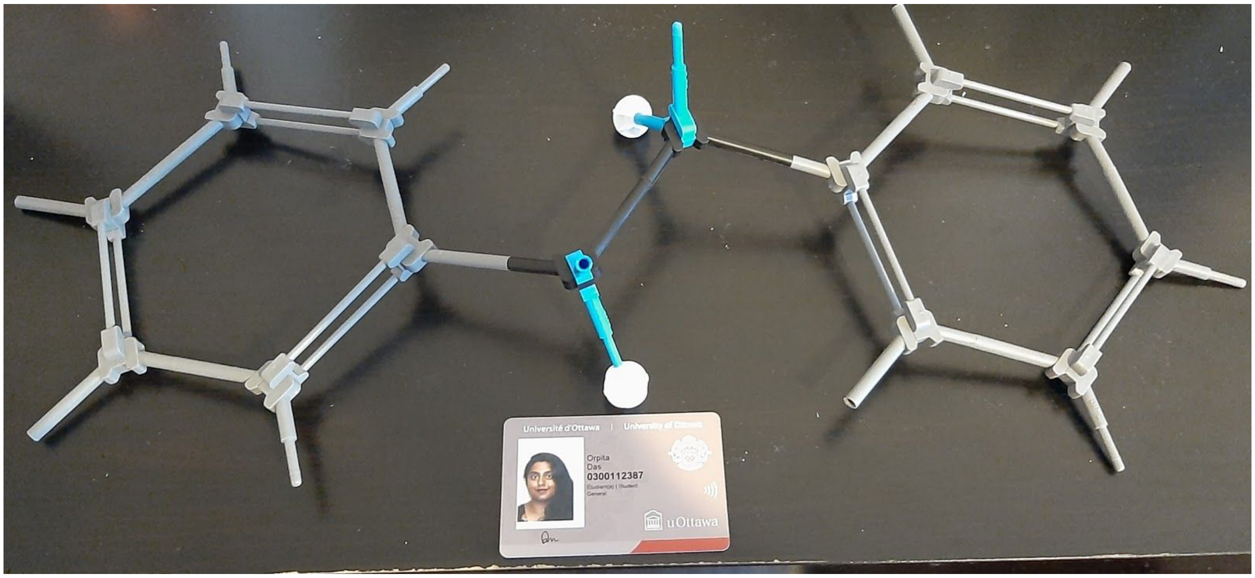
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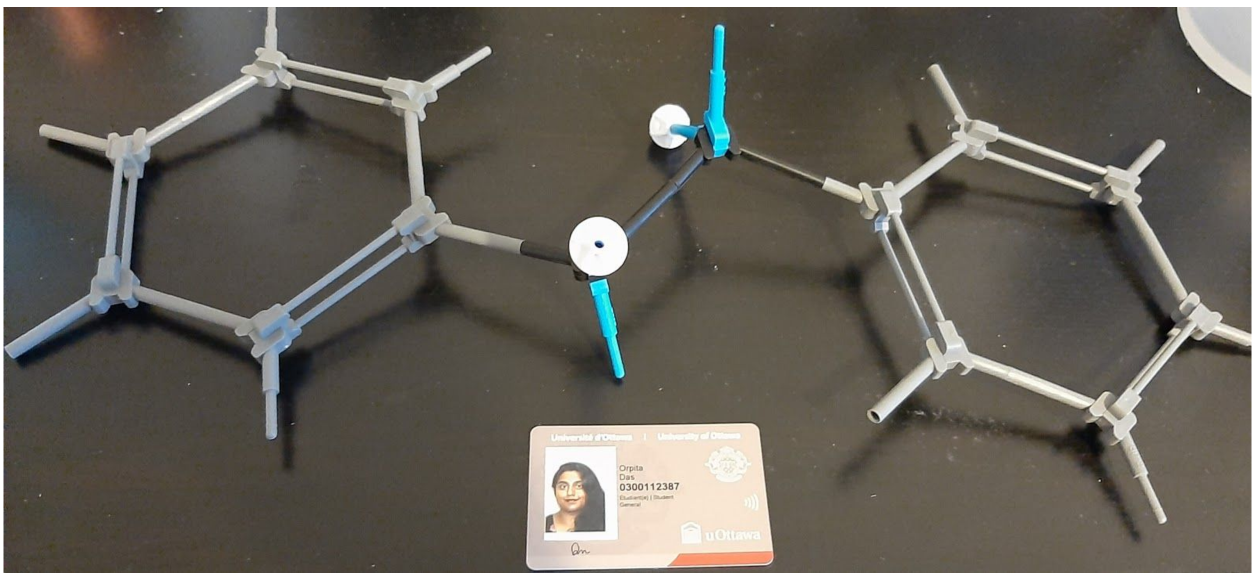
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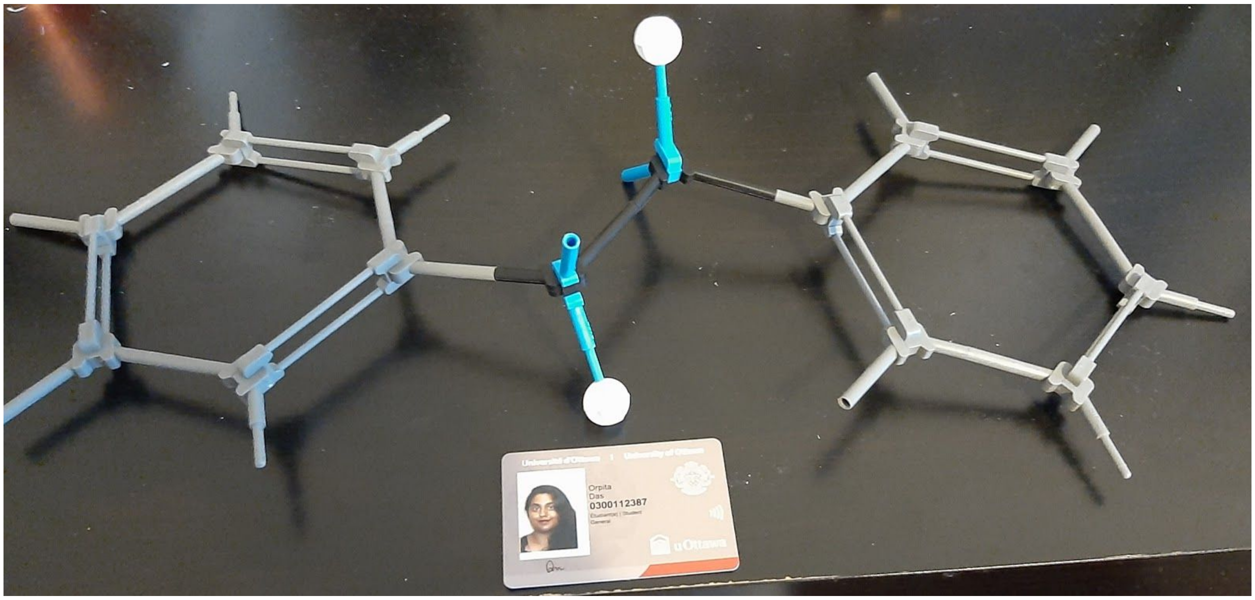
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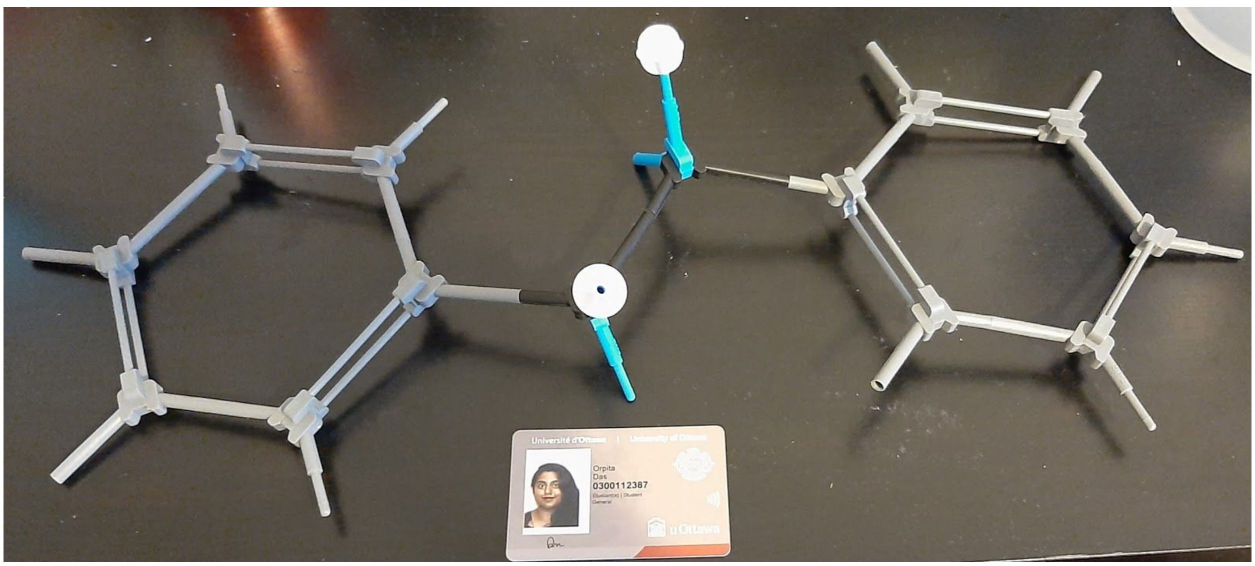
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