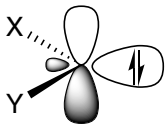
CH241 Experiment #6; Weeks of November 12 and 26, 2018
Stereochemistry of Dichlorocarbene Addition to Alkenes*

*(*This experiment was developed at Colby College with the assistance of Thu Le '19)*

Background

Carbenes are reactive intermediates featuring a neutral, divalent carbon with a pair of nonbonded electrons. A singlet carbene (**1**) has both nonbonded electrons in the same orbital with their spins paired, whereas the triplet (**2**) has each of the two nonbonded electrons occupying different orbitals with their spins unpaired.



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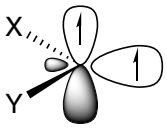

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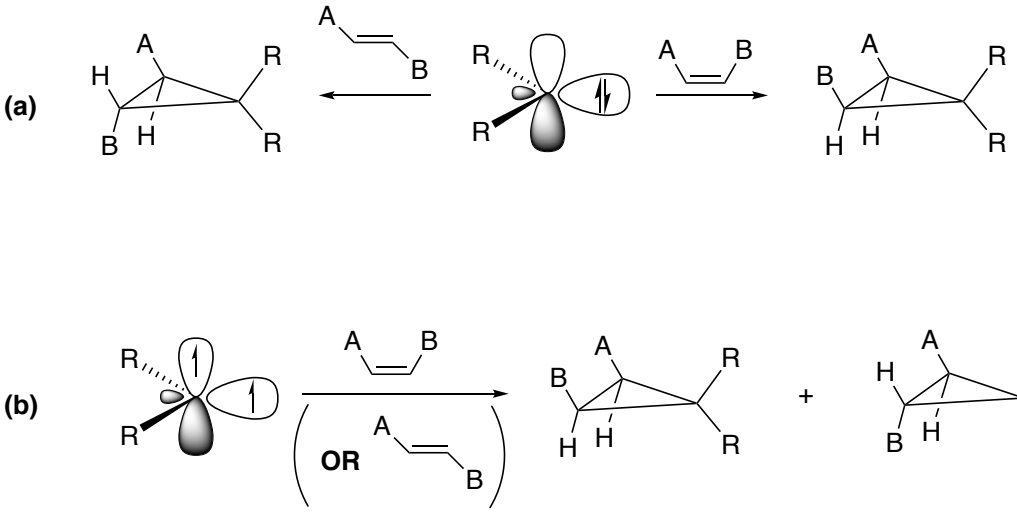
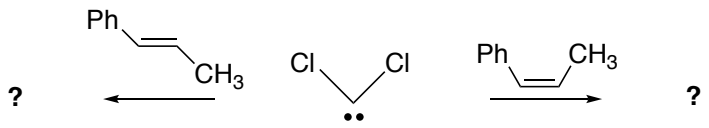
Singlet carbenes typically react with cis/trans alkenes in a single step (Scheme 1a) to form cyclopropanes in which the original stereochemistry of the alkene is preserved. Triplet carbenes can also form cyclopropanes, but by a two-step process which could lead to a scrambling of stereochemistry in the product (Scheme 1b). Thus, by comparing the stereochemistry of the cyclopropane product and starting alkene, one could determine the spin state of the reacting carbene.



Scheme 1: Typical reactions of (a) singlet and (b) triplet carbenes with *cis*- and *trans*-alkenes.

In this experiment, you will study the addition of dichlorocarbene to *cis*- or *trans*-β-methylstyrene (Scheme 2). You will then analyze the reaction mixture by ^{1}H NMR spectroscopy to ascertain the stereochemistry of the product cyclopropanes. The results of your experiments will allow you to determine the spin state of dichlorocarbene in this reaction. You will also

calculate the energies of singlet and triplet dichlorocarbene and compare your theoretical findings to the experimental results.



Scheme 2: Reaction of dichlorocarbene with *cis*- or *trans*-β-methylstyrene.

Week 1

Experimental procedure:

1. In a 20-mL vial with a thick stirring bar, add 3 mL of chloroform, 0.5 mL of the alkene (*cis*- **or** *trans*-β-methylstyrene), and 10 to 25 mg of benzyltriethylammonium chloride (TEBA)
2. Clamp the vial, set it on top of a stirring plate and start stirring
3. Using a pipet, slowly add 3 mL of a 50% NaOH solution over 3 minutes.
4. Leave the solution stirring for 1 hour. The solution should turn a light-yellow color.
5. Pour the reaction mixture into a 125-mL separatory funnel and dilute with 25 mL of water and 25 mL of dichloromethane. Separate the two layers.
6. Wash the organic layer once with 25 mL of 2M HCl, then with 25 mL of water, and finally with 25 mL of brine.
7. Dry the organic layer with anhydrous sodium sulfate and then remove the solids by filtration.
8. Remove the solvent from the filtrate using a rotary evaporator and save the residual oil in a vial for next week.

Computational studies:

Using Spartan '14, build and perform equilibrium geometry calculations for both singlet and triplet dichlorocarbene. When setting up your calculations, select Density Functional/B3LYP as your method and 6-31G* as your basis set. Also make sure to input the correct number of unpaired electrons in order to define whether the structure is in the singlet or triplet state. Record the energies of each carbene, the C–Cl bond lengths, and the Cl-C-Cl bond angles.

Week 2

Using your product from week 1, prepare a sample for ^{1}H NMR as demonstrated by your lab instructor. You will also use your left-over NMR sample for GC/MS analysis. Analyze the ^{1}H NMR and GC/MS data to answer the following questions.

(a) How did you verify the identity of the cyclopropane products?
(b) Based on the stereochemistry of the cyclopropane products, how can you determine the spin state of the reacting carbene?
(c) If your reaction did not go to completion, how can you estimate the percent conversion of alkene to cyclopropane using ^{1}H NMR spectroscopy?

Pre-laboratory Assignments

Week 1:

1. Using appropriate drawings, show how you might synthesize β-methylstyrene using an elimination reaction (you need not worry about *cis* and *trans* stereoisomers).
2. Read section 11.5 in your text.

Week 2:

1. Based on the results of your calculation from last week, predict how dichlorocarbene might react with *cis* and *trans* β-methylstyrene.
2. Explain how you might use ^{1}H NMR spectroscopy to tell the difference between *cis* and *trans* β-methylstyrene, and their cyclopropane products with dichlorocarbene.

What Should Be In Your Notebook?

1. An entry of the title, date, and page number in your table of contents.
2. An entry of the title, date, and partner's name on the first page of your experiment.
3. Masses and/or volumes of all materials that you used in this experiment.
4. Brief description of the procedures you followed for running the reaction and preparing your NMR and GC/MS samples.
5. Results of your computational studies on dichlorocarbene.
6. An estimate of how much alkene was converted into cyclopropane based on your ^{1}H NMR spectrum.
7. A description of how ^{1}H NMR spectroscopy was used to determine the stereochemistry of the cyclopropane products.

What Should Be In Your Laboratory Report?

Use the **Experiment 6 Report Form** to write your lab report.

Remember to:

1. Submit an electronic copy to CH241Lab@colby.edu by the date your report is due.
2. Submit a hardcopy in lab on the due date (start of lab).