LAB PROCEDURE:

# Green Chemistry in the Undergraduate Organic Laboratory: Microwave-Assisted Synthesis of a Natural Insecticide on Basic Montmorillonite K10 Clay

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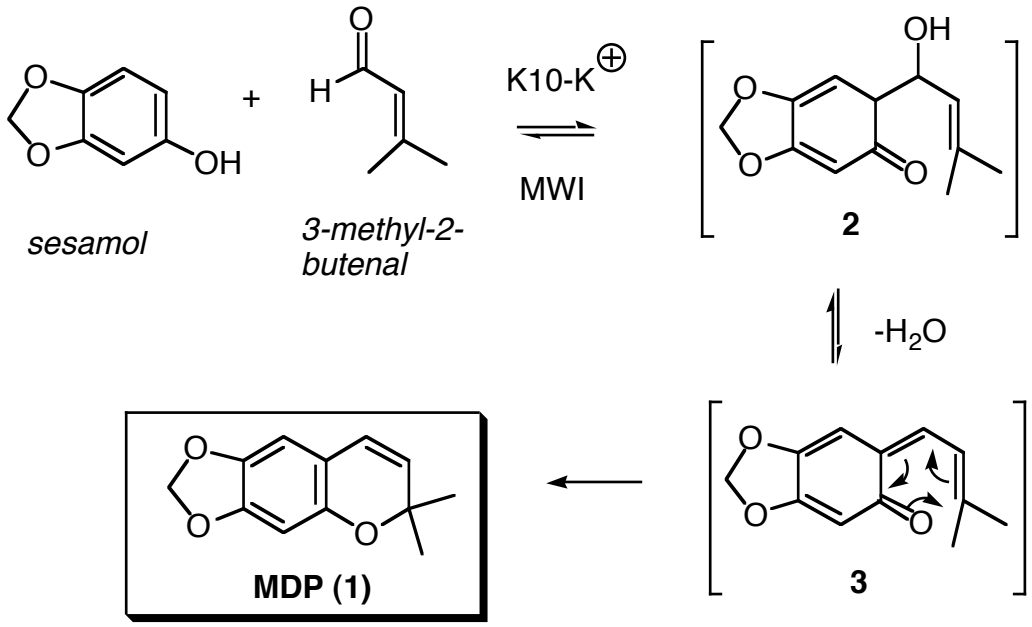
**Special Chemical Needs:** Montmorillonite K10 clay, saturated aqueous Potassium Carbonate, Sesamol, 3-Methyl-2-butenal, Ethyl acetate, 2N Sodium Hydroxide, saturated aqueous Sodium Chloride, Magnesium Sulfate.

**Safety:** Safety goggles, gloves, and a laboratory coat or apron should be worn at all times. All experiments must be performed in a fume hood. All chemicals should be considered hazardous and direct physical contact with them must be avoided. If exposed, immediately flush skin with water for at least 10 min, while contaminated clothing is removed. Do not ingest or taste any chemicals under any circumstances.

## Student Instructions

**Prelaboratory:** Search the literature and find the references related to the synthesis of methylenedioxyprecocene. Read the references and understand the mechanism pertaining to the synthetic route shown below:




**Experimental Procedure:**

*Synthesis of methylenedioxyprecocene* (**1**)

Using a balance, weigh out 500 mg of Montmorillonite K10 clay. Transfer the clay to a 50 mL Erlenmeyer flask. Using a graduated cylinder measure out 10 mL of saturated aqueous $K_2CO_3$ and add it to the flask containing the clay. Add a magnetic stir bar to the aqueous clay mixture and stir for approximately 10 min at room temperature. Meanwhile set up a vacuum filtration apparatus (side-arm Erlenmeyer flask, filter adapter, Hirsch funnel with filter paper; connect the side arm of the Erlenmeyer to an aspirator via vacuum tubing). Remove the magnetic stir bar, swirl the aqueous basic clay mixture and collect the clay by vacuum filtration. Allow the clay to dry in the Hirsch funnel for several minutes, then transfer it to a clean watch glass, spread it out with a spatula and allow it to dry in an oven at 110 °C for a period of 1 h. Carefully remove the

hot, basic clay from the oven and allow it to cool to room temperature on the watch glass in a desiccator. While the clay is cooling, weigh out the sesamol (138 mg, 1 mmol) and add it to a 20-mL disposable glass scintillation vial (Wheaton). Using a micropipet draw up the 3-methyl-2-butenal (106 μL, 1.1 mmol) and add it to the vial with the sesamol. Gently tap the vial to allow the sesamol to dissolve. To the resulting dark solution add all of the cool, dry clay and carefully distribute the mixture evenly using a metal spatula. Place the vial in the center of the carousel platform of a household grade microwave oven, cover the vial with a watch glass or other flat piece of glass, and microwave for a period of 8 minutes (several samples may be microwaved at once). Let the reaction mixture cool to room temperature. Then add 5 mL methylene chloride and gently swirl the vial. Separate the clay from the organic solution by vacuum filtration using a Hirsch funnel. Rinse the clay with two successive 5-mL portions of methylene chloride. Transfer the filtrate to a 250-mL separatory funnel and wash successively with 2 N NaOH (2 x 10 mL), and saturated aqueous NaCl (1 x 10 mL). Dry the organic phase over $MgSO_4$. Remove the drying agent by vacuum filtration. Transfer the filtrate to a tarred flask and remove the methylene chloride by gently blowing a stream of air over the crude product until mass is constant. Weigh the flask containing the crude methylenedioxyprecocene product (a dark brown, viscous oil) and calculate a percent yield. Analyze the product by TLC, GC-MS, IR, or NMR spectroscopy. Assess the purity of your product and interpret all data.

**Exercises**

1. List four advantages to using clay as a catalyst for organic reactions.

2. What is meant by the term “green chemistry”?

3. What is the purpose of using a microwave oven for this reaction?

4. Show a mechanism for the base-catalyzed reaction of sesamol with 3-methyl-2-butenal to give MDP.

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Operator : MRD
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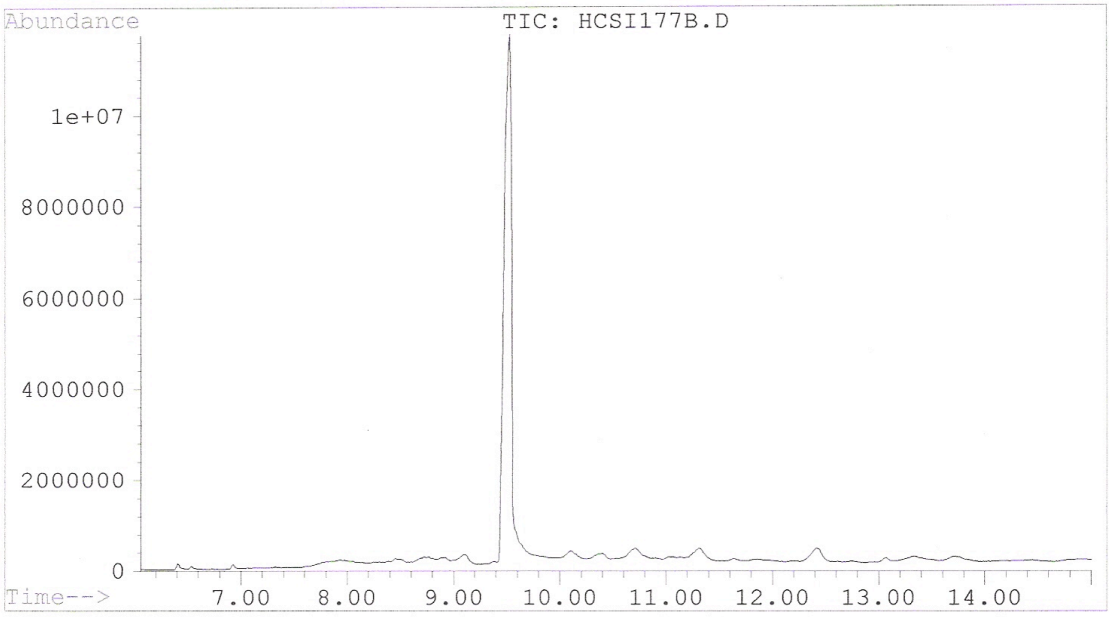
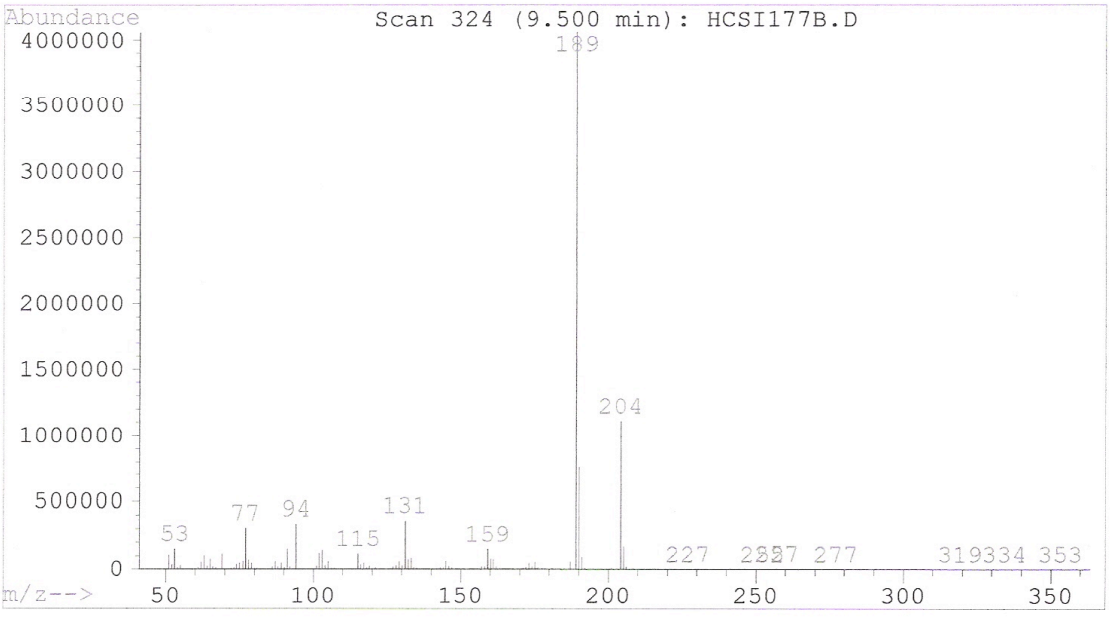
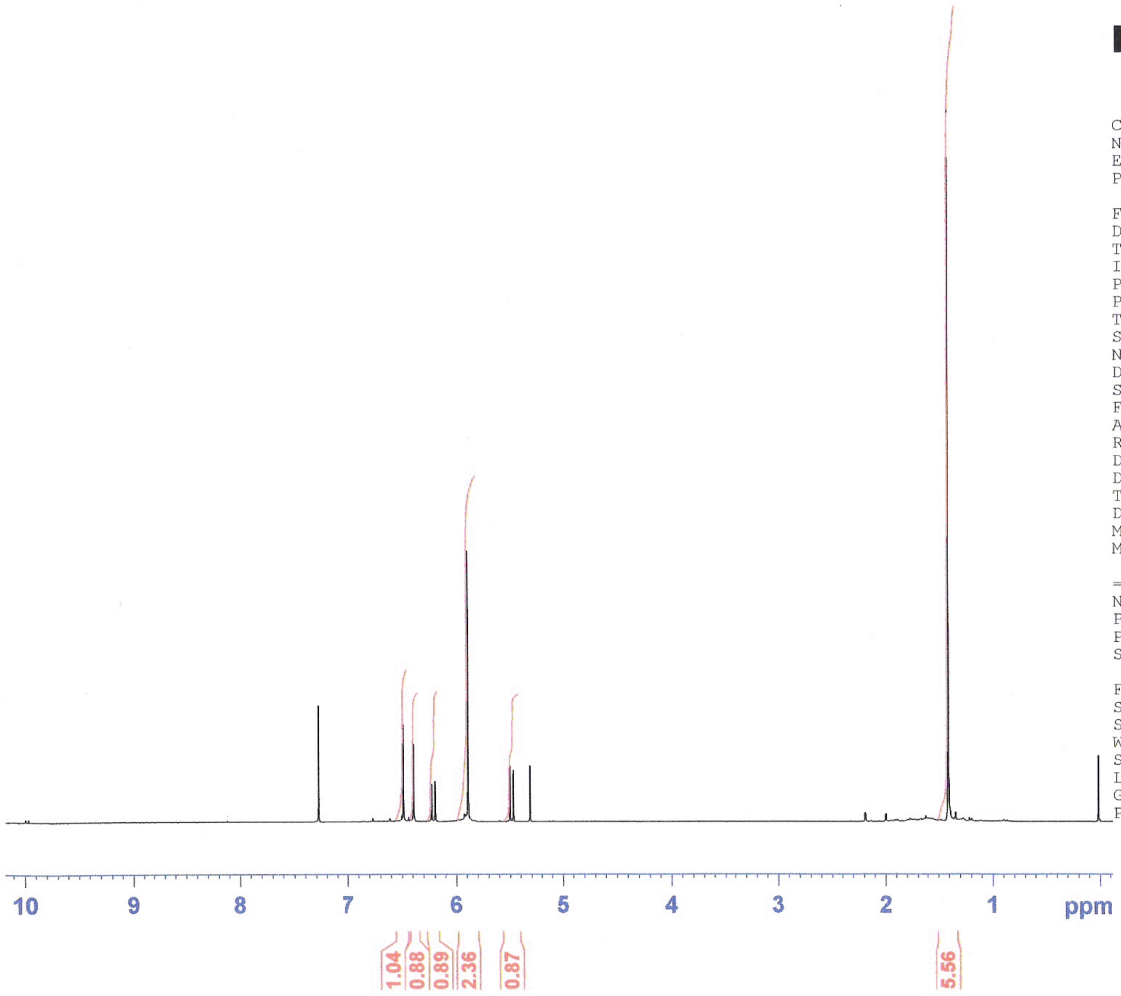
Instrument : 5971 - In
Sample Name: HCS-I-177-B
Misc Info : AFTER WORKUP W/NaOH
Vial Number: 1



HCS-I-177-B




Current Data Parameters

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| PROCNO | 1 |

F2 - Acquisition Parameters

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|---|---|
| Date_ | 20041028 |
| Time | 18.25 |
| INSTRUM | spect |
| PROBHD | 5 mm PABBO BB- |
| PULPROG | zg30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
| NS | 16 |
| DS | 2 |
| SWH | 6172.839 Hz |
| FIDRES | 0.094190 Hz |
| AQ | 5.3084660 sec |
| RG | 406.4 |
| DW | 81.000 usec |
| DE | 6.00 usec |
| TE | 0.0 K |
| D1 | 1.00000000 sec |
| MCREST | 0.00000000 sec |
| MCWRK | 0.01500000 sec |

======== CHANNEL f1 ========

| | |
|---|---|
| NUC1 | 1H |
| P1 | 12.00 usec |
| PL1 | -1.00 dB |
| SFO1 | 300.1318534 MHz |

F2 - Processing parameters

| | |
|---|---|
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| SF | 300.1300000 MHz |
| WDW | EM |
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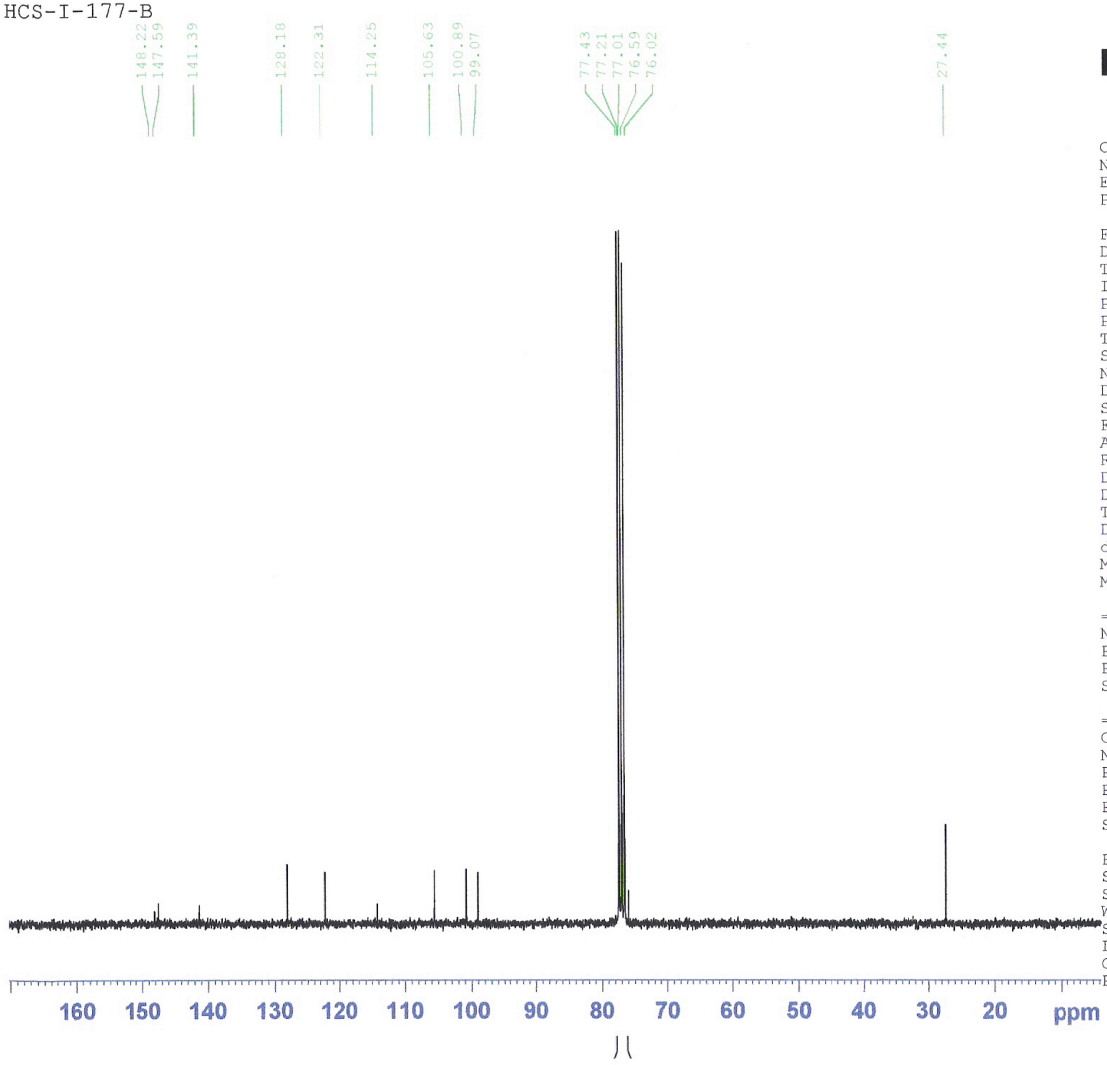
| LB | 0.30 Hz |
| GB | 0 |
| PC | 1.00 |

HCS-I-177-B

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| PROCNO | 1 |

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| PULPROG | zgig30 |
| TD | 65536 |
| SOLVENT | CDCl3 |
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| DS | 4 |
| SWH | 17985.611 Hz |
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| RG | 16384 |
| DW | 27.800 usec |
| DE | 6.00 usec |
| TE | 0.0 K |
| D1 | 2.00000000 sec |
| d11 | 0.03000000 sec |
| MCREST | 0.00000000 sec |
| MCWRK | 0.01500000 sec |

======== CHANNEL f1 ========

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|---|---|
| NUC1 | 13C |
| P1 | 8.80 usec |
| PL1 | -2.00 dB |
| SFO1 | 75.4752953 MHz |

======== CHANNEL f2 ========

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| NUC2 | 1H |
| PCPD2 | 90.00 usec |
| PL2 | -1.00 dB |
| PL12 | 17.00 dB |
| SFO2 | 300.1312005 MHz |

F2 - Processing parameters

| | |
|---|---|
| SI | 32768 |
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| WDW | EM |
| SSB | 0 |
| LB | 1.00 Hz |
| GB | 0 |
| PC | 1.00 |