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**Acetylferrocene Synthesis**

**Purpose:**

The purpose of this experiment is to monitor the acetylation of ferrocene. We will do this through a Friedel-Crafts acetylation reaction, using acetic anhydride and phosphoric acid to acetylate ferrocene to acetylferrocene.

**Reaction(s):**



**Physical Properties of Reagents**:

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Reagent | | | Structure | | Molecular Formula | | Molecular Weight (g/mol) | | Boiling Point (°C) | | Density  (g/mL) | |
| Ferrocene | | |  | | C10H10Fe | | 186.04 | | 249 | | 1.11 | |
| Acetic Anhydride | | |  | | C4H6O3 | | 102.09 | | 139.8 | | 1.08 | |
| Phosphoric acid | | |  | | H3PO4 | | 97.99 | | 158 | | 1.88 | |
| Ethyl acetate |  | | C4H8O2 | | 88.11 | | 77.1 | | 0.902 | |
| Hexane |  | | C6H14 | | 86.18 | | 68 | | 0.655 | |

**Procedure:**

Begin by acquiring the proper laboratory equipment and dressing in the proper lab attire. Commence the experiment by measuring out 0.500 grams of ferrocene using a analytical scale and weight paper. Transfer the massed out ferrocene into a 25 mL round-bottom flask with a magnetic stirring rod. Assemble a water cooling apparatus with a thermometer above a hot plate and prepare a hot water bath. Use the thermometer to monitor the temperature of the water bath. Under the fume hood, add a total of 2.0 mL of acetic anhydride and 0.3mL of 85% phosphoric acid (approximately 15 drops from a micropipette) to the 25 mL round-bottom flask containing the ferrocene. Document any observations that may prove relevant to the experiment. Following the addition of the necessary reagents, attach the 25ml round bottom flask to the water-cooled condenser and submerge the flask within the hot water bath. Utilize the stir function on the hot plate to mix the reaction. Allow the mixture to reflux for a total of 10 minutes.

Once this step has been completed, poor the mixture onto roughly 25 grams of ice in a 400 mL beaker. Use a minimum amount of distilled water to extract as much of the remaining mixture from the 25 mL beaker into the 400 mL beaker. Stir the dark orange residue within the beaker with a glass rod until any remaining ice has melted. Next, slowly add solid bicarbonate to the mixture until any remaining acid within the mixture is neutralized. Monitor the pH of the mixture by using litmus paper. Allow the mixture to settle for roughly 10 minutes. Use a Hirsch funnel and vacuum filtration to collect the solid product. Begin by pre-wetting the filter paper on the funnel and slowly adding the mixture onto the funnel over time. Once the mixture has been filtered out, allow the product to dry on the funnel for an extra 10 minutes to remove any moisture. For the purpose of this lab allow it to dry overnight due to time constraints and to remove any remaining moisture.

Conduct TLC measurements on samples of the crude product and the original ferrocene compound to find the optimal eluent to conduct column chromatography. Do this by dissolving a few crystals of each into test tubes using a minimum amount of dichloromethane. This will allow for a base reading regarding the polarity and intermolecular forces acting upon the given reagents within the given eluents. To do this, begin by collecting a silica gel TLC plate and make the appropriate markings using a pencil. Next, utilize a glass capillary tube to conduct the appropriate spotting technique of the reagents onto the silica TLC plates. One will need to place both ferrocene and the crude product on each plate. Be sure to place an appropriate distance apart from each other and from the base of the plate. Next, place an appropriate amount of eluent into a 50ml beaker using a pair of tweezers so that it will not surpass the spotted reagents prior to the spread of the eluent along TLC plate. Next place a watch glass on top of the beaker to allow for a saturated atmosphere and allow for the eluent to proceed until it reaches the solvent front. Remove the plate immediately once it reaches the front to prevent a botched reading. You will conduct this using a collection of different eluents including 100% hexane, 5% ethyl acetate/hexane mixture, and 10% ethyl acetate/hexane mixture, 20% ethyl acetate/hexane mixture, and 30% ethyl acetate/hexane mixture. Record your results of the given TLC with the help of a UV light and utilize this information to choose the best eluent while conducting your experiment.

For the given experiment, flash chromatography will be used. Prepare the glass column for the given chromatography. Set up the column using a ring stand and a clean glass column. Pack the column by adding an absorbent composed of silica gel using the slurry method containing 100% hexane. It is important to ensure that there are no bubbles present within the column to ensure a desired outcome. This layer should be roughly 8 inches in length. Run the pure hexane eluent through the column to ensure good packing. Use the hexane to ensure that there are no silica remnants on the walls of the column. Next, a thin and even layer of sand is added on the top of the absorbent layer. Allow the column to run until the eluent drops just below the sand. Dissolve the crude product using a very minimum amount of DCM. Using a micropipette, transfer as much of the dissolved crude product into the column. Allow for the sample to make its way down the column before carefully adding hexane to the column using a micropipette. Allow the column to run and collect the samples in test tubes as the column runs to completion. Be sure to not allow the column to run dry as it may allow the column to crack and ruin the chromatography. Due to the fact that flash chromatography is used, the initial eluent of 100% hexane will allow for the flushing out of the ferrocene (non-polar compound) as the acetylated product (polar compound), will remain on the top of the column. After the collected eluent begins to turn clear and the remaining ferrocene has been collected, run a TLC paper to confirm the results that no more ferrocene remains in the system. Next, complete the flash chromatography by gradually increasing the polarity of the solvent system to run out the remaining product. Run the system by adding 30mL of 5% ethyl acetate/hexane mixture followed by 30mL of 10%, 15%, 20%, and 30% ethyl acetate/hexane mixture. Be sure to collect the samples that pass through the column in test tubes. After the column has run to completion and the collected samples begin to contain a clear color use a TLC papers once again to confirm that no more product remains within the column. Perform TLC papers on the collected samples to determine which test tubes contain the acetylated product. After determining the test tubes containing the product, collect all of the samples into a 250 mL round bottom flask. Utilize rotary evaporation to collect the final product.

Using the final product that was collected run NMR, IR spectroscopy and melting point. To perform the IR spectroscopy, mix a few crystals of the final product with potassium bromide using a mortar and pastel. Use a press to make a pellet and run the IR spectroscopy. To perform the NMR sample, measure 0.030 grams of the product and dissolve in 0.7 mL of DCM. Add to a clean NMR tube and add a single drop of TMS. Use this sample to run NMR. To perform melting point, obtain a glass capillary tube and collect roughly 8mm of the sample into the tube by gently tapping the tube against the sample. Insert the capillary tube into the melting point apparatus and carefully monitor the reading.

**Observation:**

Initial: Ferrocene vibrant orange color

Reflux for 10 minutes: Mixture turned Dark Brown/ Reddish

Pouring over ice bath: Blackish mixture with orange precipitates collecting at the bottom

After filtration funnel: Vibrant orange solid collected on the top and orange liquid collected in flask

Crude Product in column: Bands present throughout the column, yellowish ferrocene separated first with pure hexane eluent. Dark band remained on top until a more polar eluent was introduced.

Collected test tube samples: Ferrocene samples were light yellow while acetylated product was darker orange color

**Data/Results:** See Notes for Calculations

* Theoretical yield:
  + Start: 0.500 grams ferrocene
  + Yield: 0.613 grams of acetylferrocene
* Actual yield and % yield of the final product.
  + Actual Yield: Net recovery of 0.523 grams of final product (acetylferrocene)
* Percent Yield
  + = 85.32% recovery
* Flash Column Chromatography data:
  + Eluents: 100% Hexane until all remaining ferrocene was removed
  + 30mL of increasing polar eluents
    - 5%, 10%, 15%, 20%, and 30% ethyl acetate/hexane mixtures
  + 27 fractions collected
  + Fractions 18-26 contained the final product confirmed by TLC
* Melting Point
  + Theoretical: 81oC-83oC
  + Experimental: 82oC-85oC
* IR spectrum absorption bands
  + C(sp2)-H aromatic stretch: 3093.2 cm-1
  + C(sp3)-H: 1458.18 cm-1, 1357.89 cm-1
  + C=O stretch: 1658 cm-1
  + =C-H bend 825.53 cm-1
* 1H NMR spectrum

|  |  |  |
| --- | --- | --- |
| Proton (s) | Chemical Shift (ppm) | Coupling |
| A | 2.393 | Singlet |
| B | 4.770 | Triplet |
| C | 4.499 | Triplet |
| D | 4.202 | Singlet |

* TLC Data: See Notes for Diagrams and Calculations
  + TLC (100% Hexane) Rf Values:
    - Ferrocene 1.1 cm/2.70 cm=0.41 cm
    - Acetylferrocene: No Movement
  + TLC (5% ethyl acetate/hexane) Rf Values:
    - Ferrocene: 2.20 cm/2.80 cm= 0.79 cm
    - Acetylferrocene 0.3 cm/2.80cm= 0.11 cm
  + TLC (10% ethyl acetate/hexane) Rf Values:
    - Ferrocene: 2.4 cm/2.7 cm= 0.89 cm
    - Acetylferrocene: 0.7cm/ 2.7cm= 0.26 cm
  + TLC (20% ethyl acetate/hexane) Rf Values:
    - Ferrocene: 2.8 cm/3.1 cm= 0.90 cm
    - Acetylferrocene: 1.2 cm/ 3.1 cm= 0.39 cm

**Discussion:**

Based on the results that were achieved throughout the experiment, it may be concluded that we were able to successfully perform a Friedel-Crafts acetylation reaction through the acetylation of ferrocene. First, by looking at our percent yield we were able to receive a favorable yield of 85.32%. We received a net yield of 0.523 grams with an expected yield of 0.613 grams. Additionally, our results further go to prove the reliability of our experiment through our IR spectroscopy readings. As seen from the absorption bands received from the IR spectroscopy such as the C(sp2)-H aromatic stretch at 3093.2 cm-1, the C=O stretch at 1658 cm-1, the C(sp3)-H stretch at 1458.18 cm-1 and 1357.89 cm-1, and the =C-H bend at 825.53 cm-1 we can conclude that these bands help to confirm the structure of our acetylated compound. Additionally, the results received from the NMR reading help to confirm the positions of the hydrogen protons within the compound. This is shown from the diagram in which we are able to match the singlet of the hydrogen atoms near the acetyl group with the chemical shift of 2.393 ppm as well as the triplet of the the hydrogen atoms located on the aromatic carbon next to the acetyl group with the chemical shift of 4.770 ppm. Finally, the results are further proven reliable with the measurement of the melting point with a range from 82oC-85oC while the theoretical value is very close with a measurement of 81oC-83oC.

Despite performing a seemingly successful acetylation of ferrocene, there were a few potential sources of error that may have affected the results of our experiment. One potential source of error that may have persisted throughout the experiment was a loss of product amongst the frequent transfers between beakers, flasks, columns and pipettes. Due to this there is no certain way to completely recover the full yield of the product. Additionally, another potential source of error that may have negatively affected our results is a potential crack in the column. It appeared that there may have been a dry spot in the column. This could have potentially altered the results of our chromatography but TLC readings confirmed that the results were adequate. One improvement that I would suggest to improve this experiment would be to acetylate a colorless compound so that it would be harder to distinguish between the bands and rely more heavily on TLC chromatography to further our skills.