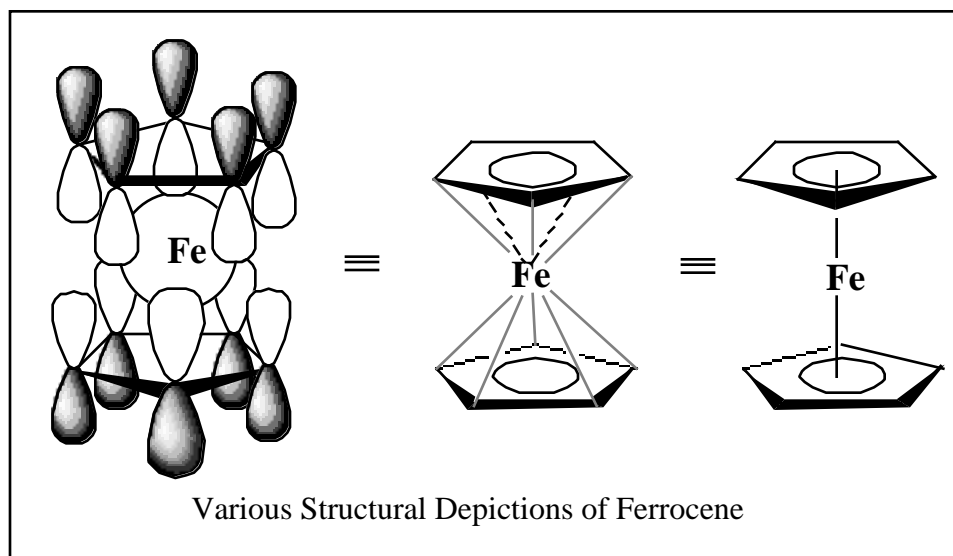


Friedel-Crafts Acylation of Ferrocene

I. Introduction

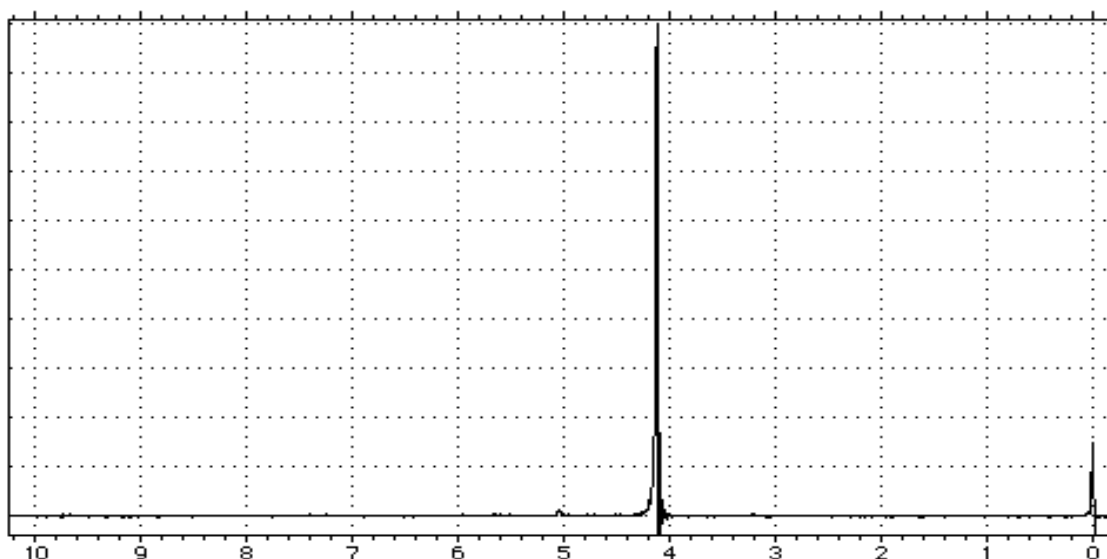
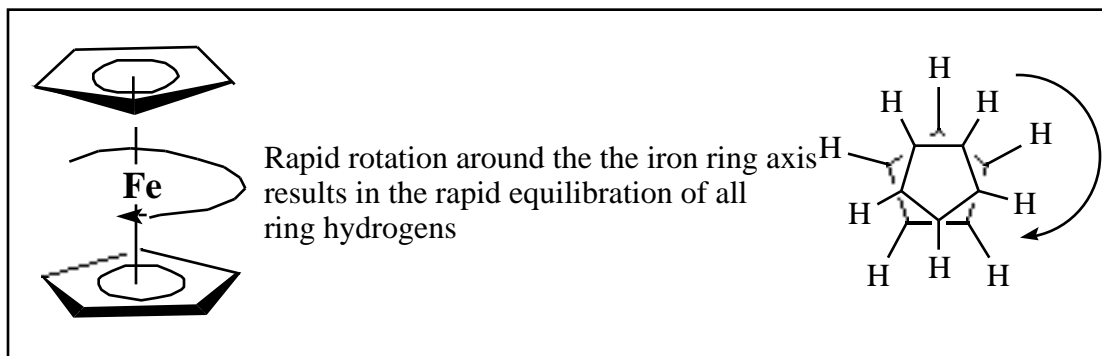
A fortunate accident in 1951 led to the discovery of an extraordinary organoiron compound, dicyclopentadienyliron, which later became known as ferrocene. Studies of this remarkably stable and atypical organometallic compound led to the determination of its structure as a combination of two cyclopentadienide anions with a ferrous (Fe^{+2}) cation. The bonding involves the six π -electrons of each of the aromatic cyclopentadienide anions in a way that binds each carbon in the rings equally to the metal. In this rather flat, sandwich-type" structure, 12 electrons from the two rings and six electrons from the iron atom lead to the very stable 18 electron configuration of the inert gas Krypton. Ferrocene is stable to 450° , soluble in organic solvents and insoluble in water.



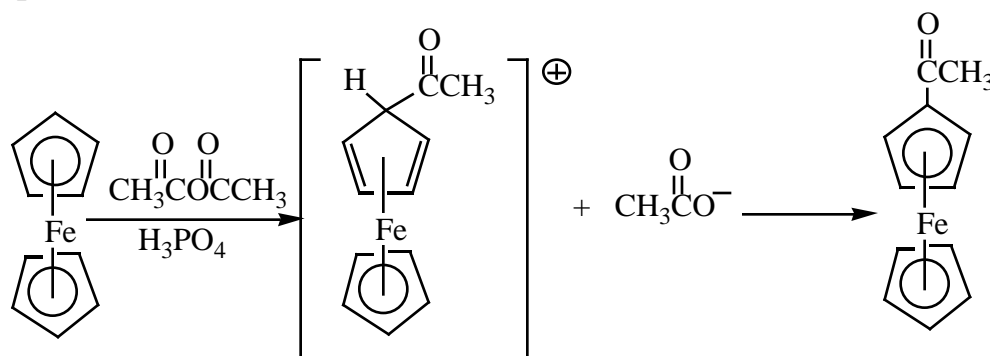
The cyclopentadienyl rings of ferrocene are electronically analogous to benzene rings in that they are aromatic six π -electron rings. Thus the chemistry of ferrocene resembles that of benzene; it undergoes various electrophilic substitution reactions even more easily than benzene because the anionic character of the five-membered rings makes them quite nucleophilic. The rate of Friedel-Crafts acylation of ferrocene is about 60 X faster than benzene. However, ferrocene is somewhat limited for use in synthetic applications, because of its relative ease of oxidation (even by the O_2 in air) which results in the blue-colored ferricinium cation.

Ferrocene is soluble in CDCl_3 and its NMR spectrum can be taken quite easily. The proton nmr spectrum for ferrocene (as shown below) consists of a single resonance peak at about 4.1 ppm. Although this resonance is 3 ppm upfield from a typical proton resonance in benzene, this difference is not the result in any decrease in aromaticity, but rather is explained by the fact that the higher electron density of the anionic rings result in greater shielding of the ring hydrogens. The

single resonance illustrates that all of the ring hydrogens are in an equivalent chemical environment.



Ferrocene can be acetylated by heating with a mixture of acetic anhydride and 85% phosphoric acid (H_3PO_4) as a catalyst. The conditions of this experiment are designed to enhance conversion to mono-acetylferrocene and diminish further acetylation to give 1,1'-diacetyl-ferrocene (this compound has two acetyl groups, one on each ring). Although an excess of acetylating agent is used, the extent of the reaction is controlled by limiting the reaction time. Unchanged ferrocene and any diacetyl derivative are removed by column chromatography using alumina as the stationary phase.



II. Experimental Procedure

Friedel-Crafts Acetylation Procedure

Fit a 50 mL round-bottom flask with a reflux condenser. In the flask place 1.0 g (0.0055 mol) of ferrocene and 10.0 mL (0.11 mol) of acetic anhydride (CAUTION: acetic anhydride is a caustic liquid with irritating vapors). To the reaction mixture slowly add 2.0 mL of 85% H_3PO_4 and then carefully swirl the reaction mixture. Heat the reaction using an external sand bath set to 90°C for 10 min. Allow the mixture to cool for 10 min and then pour it onto about 75 g of ice in a large beaker. Neutralize the mixture by portionwise addition of 6 M NaOH solution until pH paper indicates the solution is neutral (should take about 35 mL). When the mixture has cooled to room temperature, collect the solid product by suction filtration and dry it by drawing air through the filter for about 15 min. Determine the weight of crude product and purify by column chromatography

Column Chromatography

Before starting this procedure read the discussion on column chromatography in Ault (pp 120-126).

The proper preparation of a chromatography column is critical to its success. If the absorbent has cracks, channels, or air bubbles, or if it has an irregular or non-horizontal surface, obtaining a good separation will be difficult. Prepare a chromatography column by the following procedure.

1. Obtain a chromatography column from the stockroom. It should have a sintered glass plug and a length of tubing attached. Use your screw clamp to close off the tubing. Clamp this column securely to a ring stand.
2. Fill the column $\frac{3}{4}$ of the way full with the eluting solvent (cyclohexane), open the screw clamp and drain a small amount of the solvent from the column.
3. Slowly add the absorbent (40-50 g of Alumina), in a slow steady stream. As you do this, gently tap the column continuously with a piece of pressure tubing so that the absorbent settles evenly and uniformly. It is very important that there be no cracks, channels or air bubbles present. If necessary, drain some of the solvent so as to prevent the column from overflowing. However do not drain so much that the top of the absorbent becomes uncovered. At the end, make sure that the top of the absorbent is level and has no irregularities.

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4. Add a small layer of sand (about 0.5 in) to the top of the column to protect the column. Be sure to add carefully so as to not disturb the top of the column.
 5. Drain the solvent from the column so as to lower the level of the solvent to **just above** the sand layer. **Do not let the solvent level to fall below the top of the absorbent layer. The column is now ready for operation.**
 6. Carefully pipette a solution of the crude acetylferrocene dissolved in a minimal amount of toluene (about 3 mL), ignoring any resinous or insoluble byproducts, onto the top of the column. Open the stopcock and drain the liquid down to the level of the sand. Wash the flask with an additional 3 mL of toluene and again open the stopcock so that the liquid level is again just above the level of the sand.
 7. Carefully fill the column with petroleum ether (do not disturb the absorbent column). Open the clamp and begin to collect the solvent as it comes off the column. Liquid should flow out at a rate of 1-2 mL per minute. As the liquid level in the column falls below 3/4 level, add more solvent.
 8. Continue the elution, the unreacted ferrocene will move down the column first as a yellow-orange band. When the ferrocene has exited out the bottom of the column, change solvents to a 1:1 mixture of petroleum ether and ethyl acetate. This much more polar solvent will cause the acetylferrocenes to move down the column as an orange-red band.

Evaporate the colored fractions in the hood on the hot plate. Obtain the weight of each fraction. Determine the mp of each fraction. The recorded melting points are: ferrocene, 173°; acetylferrocene, 85°; diacetylferrocene, 130-131°. Take a proton nmr spectrum of your sample of acetylferrocene, assign all resonances and report whether your spectrum matches what you would expect for acetylferrocene.

III. Report

1. Cover sheet with experiment title and name
2. Introduction and experimental description
3. Observation and data, include
 - a. Wt of crude product, wt of each fraction obtained after column chromatography.
 - b. % Yield of acetylferrocene and diacetylferrocene (if present)
% recovery of any unreacted ferrocene
 - c. mp range of each fraction recovered.
 - d. nmr analysis of acetylferrocene