ANASAZI **EXPERIMENT SERIES**

FRIEDEL CRAFTS ACETYLATION OF FERROCENE

Anasazi Instruments

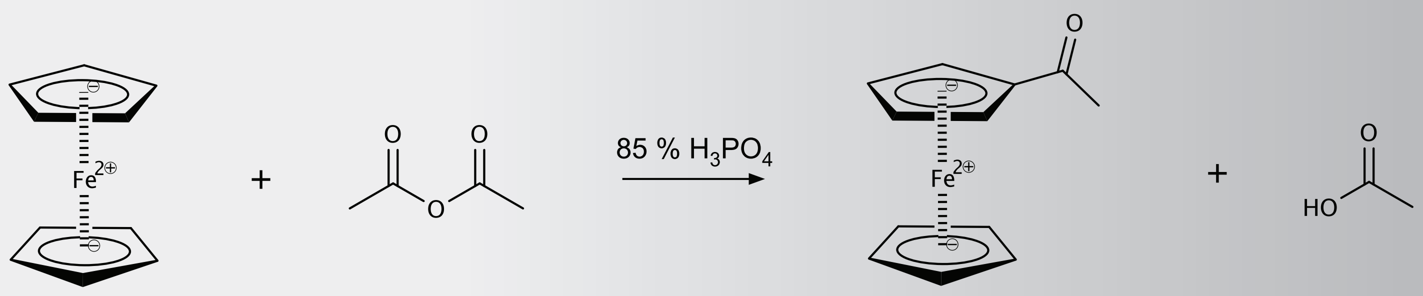
DID YOU KNOW?

The discovery of the structure of ferrocene started a revolution in organometallic chemistry.
As a result, Ernst Otto Fischer and Geoffrey Wilkinson shared the 1973 Nobel Prize in Chemistry.

Organometallic compounds are often used as advanced catalysts to synthesize a wide range of useful molecules. Sustainable polymers, synthetic fuels, and bioactive molecules can all be made with metallocene catalysts.

Do the reaction below and follow in the footsteps of chemistry giants!

THE REACTION



THE MECHANISM

Acetic anhydride and phosphoric acid react to form the acylium ion electrophile.
The nucleophile ferrocene attacks the electrophile giving acetylferrocene.

STEP 1 Protonation of acetic anhydride with phosphoric acid

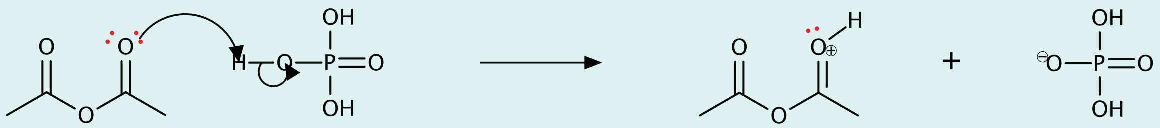
STEP 2 Cleavage of C-O bond to form acetic acid and acylium ion

STEP 3 Electrophilic aromatic substitution of H on ferrocene with acylium ion

THE MECHANISM

1

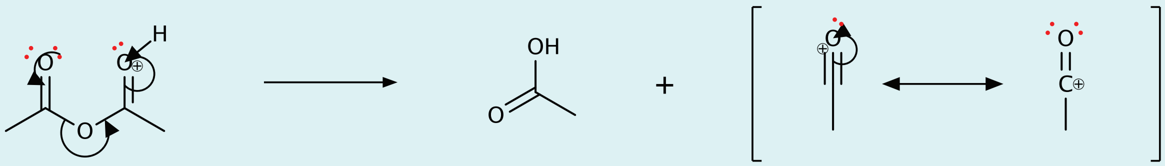
Phosphoric acid protonates acetic anhydride



2

Acetic acid leaves to form acylium ion

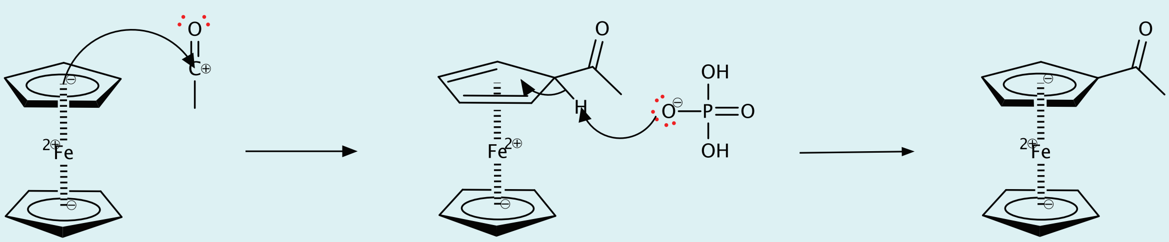
Acylium ion resonance



3

Aromatic π electrons attack acylium ion electrophile

Conjugate base removes proton from ring and restores aromaticity



REINFORCE KEY CONCEPTS

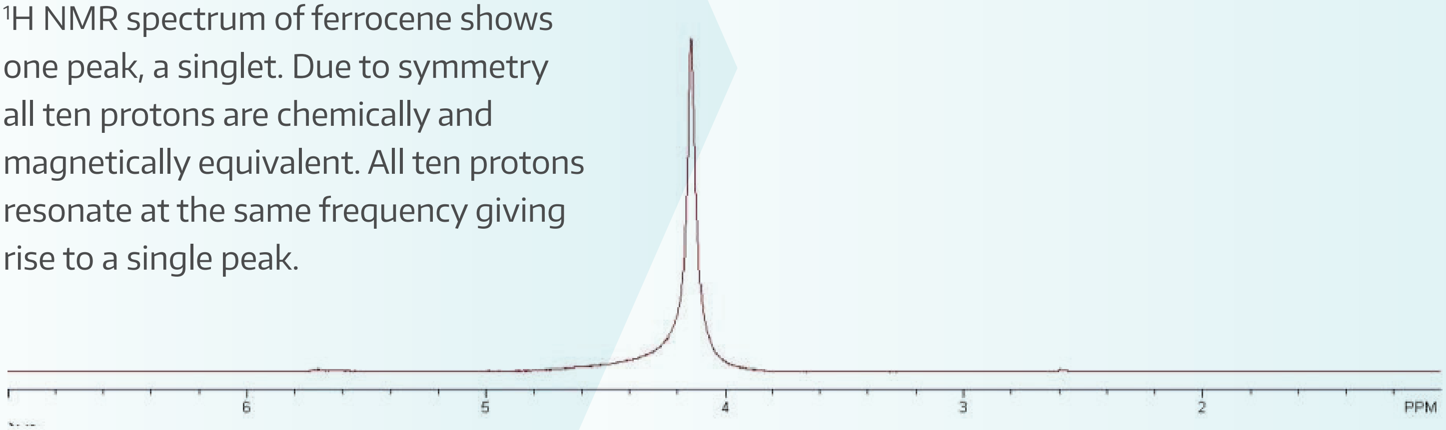
+ aromaticity
+ electrophile
+ nucleophile
+ electronegativity
+ shielding/deshielding

SPECTRA & INTERPRETATION

Ferrocene ^{1}H NMR

(60 MHz, 2 scans, 22 seconds)

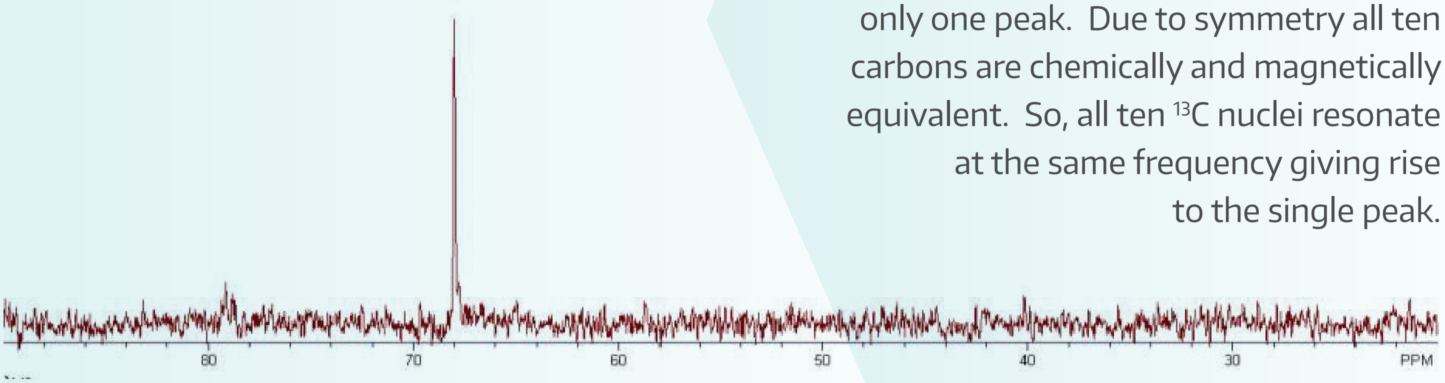
^{1}H NMR spectrum of ferrocene shows one peak, a singlet. Due to symmetry all ten protons are chemically and magnetically equivalent. All ten protons resonate at the same frequency giving rise to a single peak.



Ferrocene ^{13}C NMR

(15 MHz, 12 scans, 87 seconds)

^{13}C NMR spectrum of ferrocene shows only one peak. Due to symmetry all ten carbons are chemically and magnetically equivalent. So, all ten ^{13}C nuclei resonate at the same frequency giving rise to the single peak.

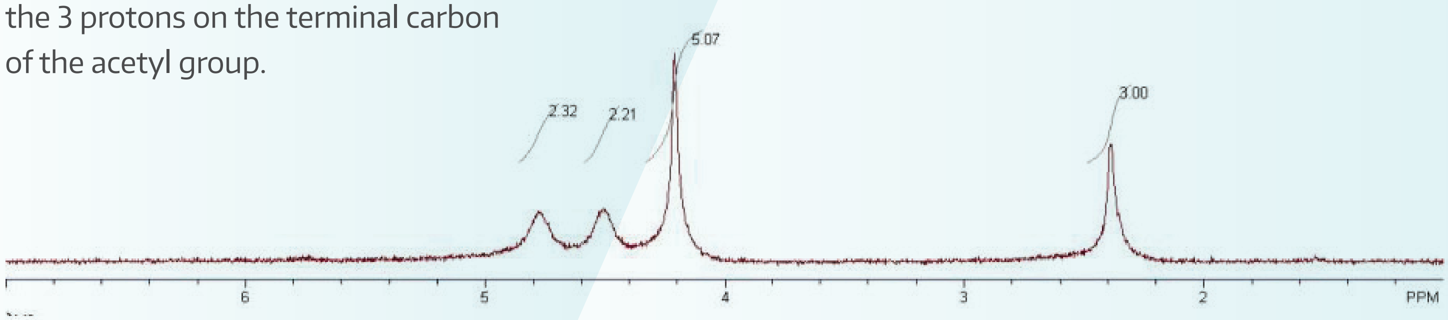


SPECTRA & INTERPRETATION

Acetylferrocene ¹H NMR
(60 MHz, 4 scans, 45 seconds)

After monoacylation the 1H spectrum changes considerably. The spectrum now shows 4 signals. The three peaks at 4.2, 4.5 and 4.8 ppm arise from the 9 protons directly attached to the ferrocene carbons. The peak at 2.4 ppm arises from the 3 protons on the terminal carbon of the acetyl group.

Integration of the signals and the deshielding effect of the acetyl group help further identification. The downfield signal at 4.8 ppm arises from two protons adjacent to the acetyl group. The signal at 4.5 ppm arises from the remaining two protons on the substituted ring. Finally the signal at 4.2 ppm arises from the 5 magnetically identical protons on the unsubstituted ring.



Acetylferrocene ¹³C NMR
(15 MHz, 256 scans, 31 minutes)

After monoacylation the ten carbon nuclei in ferrocene are no longer magnetically equivalent. As in the ¹H spectrum above, the acetyl group deshields some of the carbon nuclei giving rise to multiple signals. The three signals at 69.2, 69.5 and 72.0 ppm arise from 9 carbon nuclei in ferrocene that have an attached proton. The signal at 27.1 ppm arises from the terminal carbon of the acetyl group.

Note that the peaks at 75, 77, and 79 arise from $CDCl_3$ (J_{C-D} = 32 Hz).