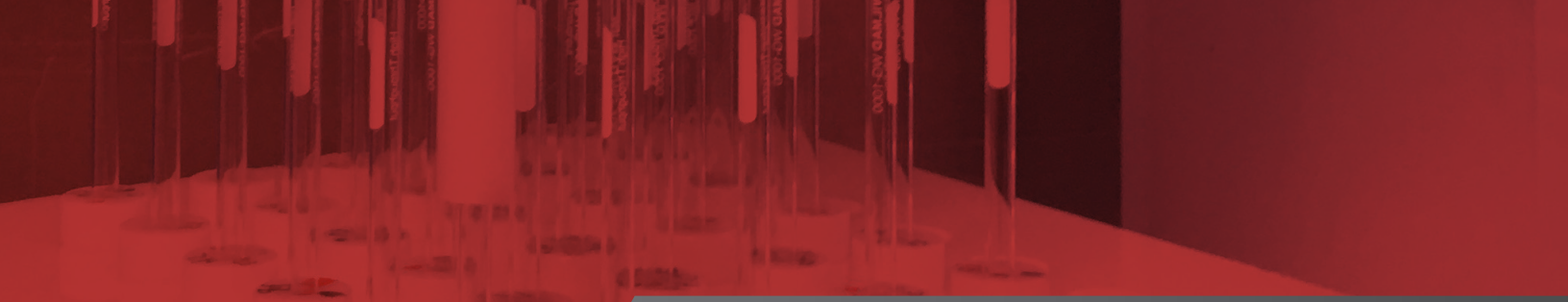


ANASAZI **EXPERIMENT SERIES**

ELECTROPHILIC AROMATIC SUBSTITUTION

NITRATION OF METHYL BENZOATE

Anasazi Instruments

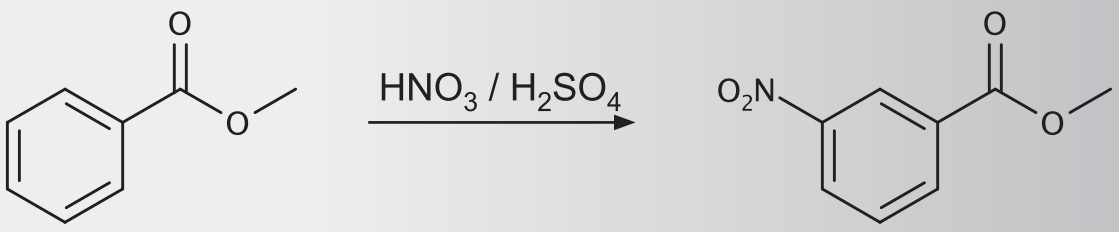
DID YOU KNOW?

The nitrogen in industrial nitric acid originates in the air you breathe, which contains 78 % nitrogen.

Much of the nitrogen in the food we eat comes from synthetic fertilizers manufactured using nitric acid.

Aromatic nitro compounds are used as explosives, antibiotics, and synthetic intermediates in the production of dyes, foams, analgesics, antidegradants for rubber, and synthetic fibers.

THE REACTION



THE MECHANISM

Nitric and sulfuric acid react to form the nitronium ion electrophile.
Nucleophilic π electrons attack the nitronium ion giving methyl 3-nitrobenzoate.

STEP 1 Sulfuric acid protonates nitric acid

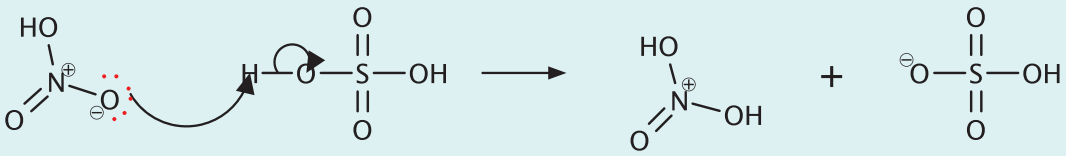
STEP 2 Water leaves protonated nitric acid forming nitronium ion

STEP 3 Aromatic π electrons attack the nitronium ion electrophile

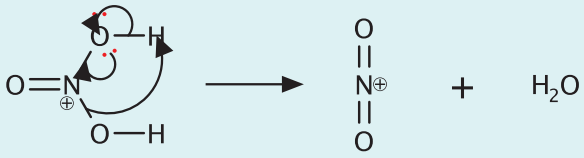
STEP 4 Conjugate base removes proton from ring restoring aromaticity

THE MECHANISM

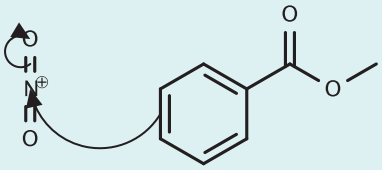
1 Sulfuric acid protonates nitric acid



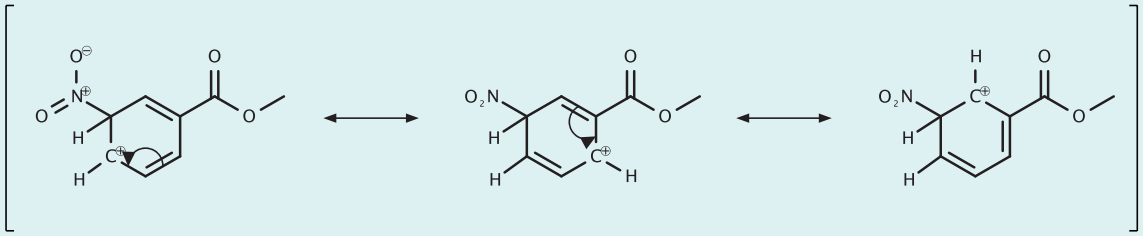
2 Water leaves to form nitronium ion



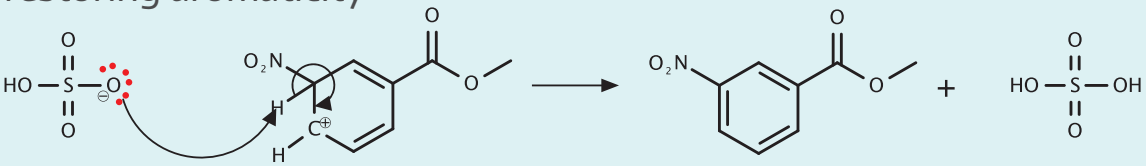
3 Aromatic π electrons attack nitronium ion electrophile



Resonance structures



4 Conjugate base removes proton from ring thus restoring aromaticity

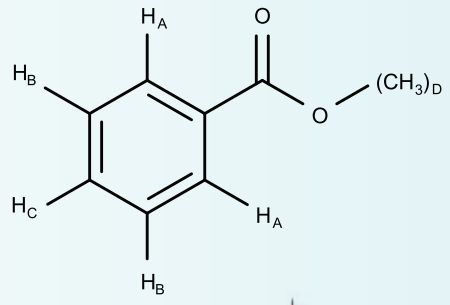


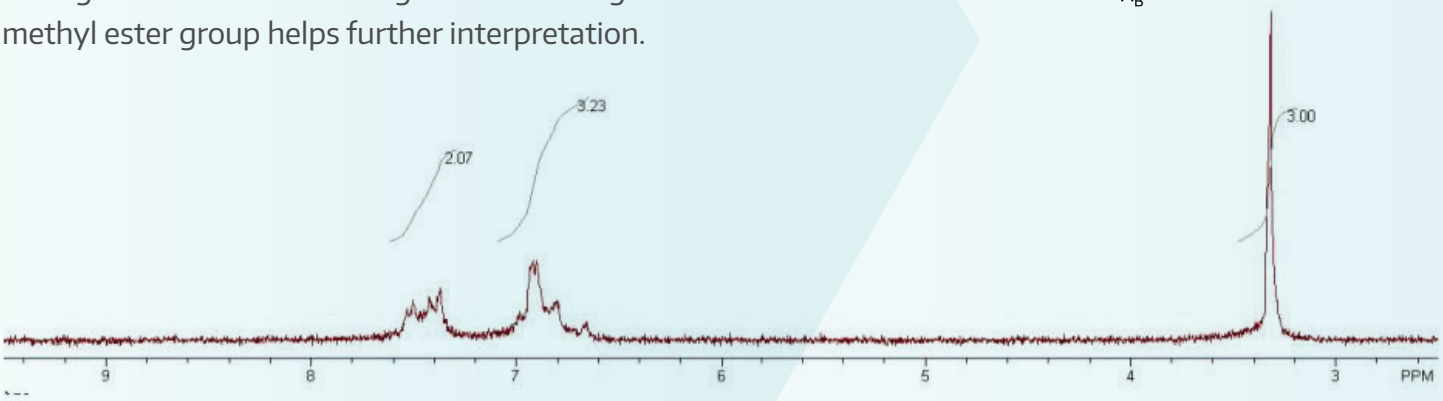
SPECTRA & INTERPRETATION

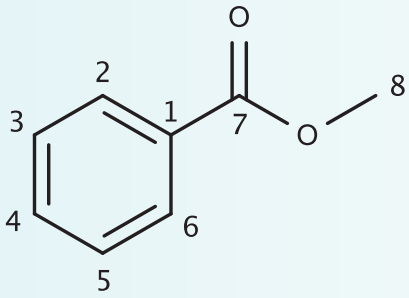
Methyl benzoate ^{1}H NMR

(60 MHz, 1 scan, 11 seconds)

^{1}H NMR spectrum of methyl benzoate shows two multiplets in the aromatic region and one singlet upfield. Integration of the signals and understanding the deshielding effect of the methyl ester group helps further interpretation.



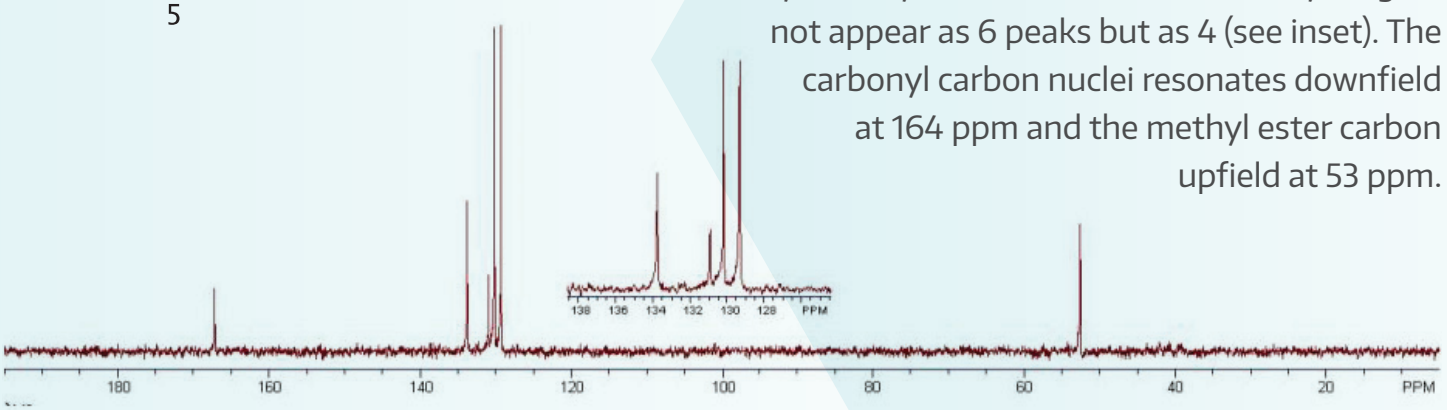




Methyl benzoate ^{13}C NMR

(15 MHz, 30° pulse, 64 scans, 8 minutes)

Because methyl benzoate possesses symmetry, the 6 carbons of the benzyl ring do not appear as 6 peaks but as 4 (see inset). The carbonyl carbon nuclei resonates downfield at 164 ppm and the methyl ester carbon upfield at 53 ppm.

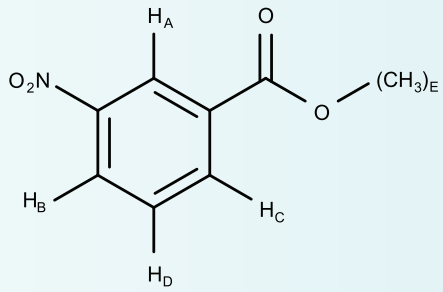


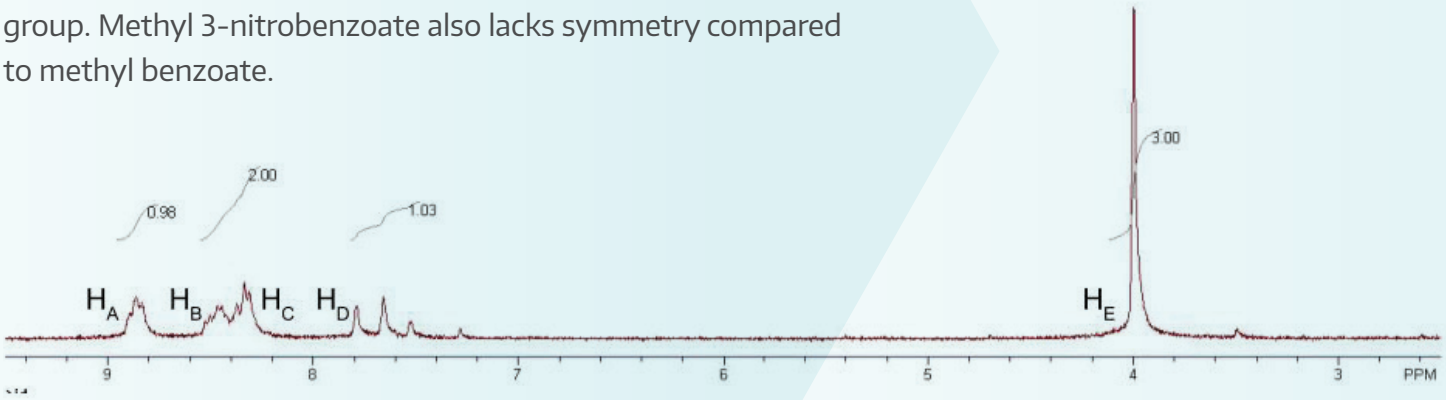
SPECTRA & INTERPRETATION

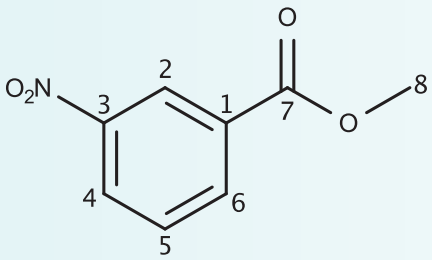
Methyl 3-nitrobenzoate ^{1}H NMR

(60 MHz, 2 scans, 22 seconds)

The nitro group is a strong electron withdrawing group and enhances the preexisting deshielding from the methyl ester group. Methyl 3-nitrobenzoate also lacks symmetry compared to methyl benzoate.







Methyl 3-nitrobenzoate ^{13}C NMR

(15 MHz, 30° pulse, 256 scans, 31 minutes)

Loss of symmetry means that the 6 carbons of the benzyl ring now resonante as 6 signals. No two carbon nuclei are magnetically equivalent. As in methyl benzoate, the carbonyl carbon resonantes downfield at 164 ppm and the methyl ester carbon resonantes upfield at 52 ppm.