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The Discovery-Oriented Approach to Organic Chemistry 1. Nitration of Unknown Organic Compounds. An Exercise in ^1H NMR and ^{13}C NMR Spectroscopy for Sophomore Organic Laboratories

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The Discovery-Oriented Approach to Organic Chemistry

1. Nitration of Unknown Organic Compounds

An Exercise in ^1H NMR and ^{13}C NMR Spectroscopy
for Sophomore Organic Laboratories

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There is increasing recognition that the discovery approach to learning is far more effective than repetition of simple cookbook experiments (1, 2). In spite of this recognition, a vast number of such experiments can still be found in most organic chemistry lab curricula. Nitration is one of the most fundamental reactions in organic chemistry. However, the majority of nitration experiments found in the standard lab textbooks are of the cookbook variety and convey none of the excitement associated with discovery in experimental chemistry (3).

We have developed some simple nitration experiments that present the student with a puzzle and are a good exercise in ^1H NMR and ^{13}C NMR spectroscopy. ^{13}C NMR spectroscopy is a powerful structure elucidation tool and yet not many examples of the use of ^{13}C NMR spectroscopy in organic lab experiments can be found (4).

Overview of the Experiment

The experiments involve nitration of unknown mono-substituted benzenes and product analysis by ^1H NMR and ^{13}C NMR spectroscopy. The nitration can be completed in an hour, and by using the appropriate solvent, it is possible to obtain good quality ^1H NMR and ^{13}C NMR spectra in 15 min per student. Product of sufficient purity is obtained without the need for recrystallization. The experiment can be extended to include other unknowns for which nitration procedures have been developed. In spite of the simplicity of the experiment, the element of discovery insures that student interest and enthusiasm are retained.

Each team of two students is assigned an unknown monosubstituted benzene.¹ Nitration is carried out and the product is analyzed by both ^1H and ^{13}C NMR spectroscopy. Students are then asked to answer a series of questions that require interpretation of the NMR spectra. This enables them to discover the structure of the starting unknown.

Discussion

Students answer the following questions related to the NMR spectra.

How many different peaks can be seen in the ^{13}C NMR spectrum (ignoring solvent and TMS)?

How many benzene ring carbons can be seen in the ^{13}C NMR spectrum?

On the basis of this information, it is possible to rule out the formation of the para isomer. Only ortho and meta nitro-substituted isomers will show 6 peaks in the aromatic region, which are seen in all the ^{13}C spectra.

Are there any other carbons in the ^{13}C spectrum? If so, what is the likely functional group based on the chemical shift in the ^{13}C NMR spectrum?

On the basis of ^1H NMR, what is the nature of the substituent?

The integration of the ^1H NMR spectrum is critical to elucidating the structure of the X group.

Experimental Procedure and Results

General Aspects

^1H and ^{13}C NMR spectra were recorded on a JEOL NMR spectrometer at 270 MHz and 67.5 MHz, respectively. The abbreviations s, d, t, q, m and br used to describe ^1H spectra refer to singlet, doublet, triplet, quartet, multiplet, and broad, respectively. Some multiplets in ^1H NMR spectra are characterized as apparent (app). This refers only to their appearance and may be an oversimplification. All chemicals used were reagent grade and were used as obtained. Nitric acid (15.8 M) and sulfuric acid were purchased from Fisher Scientific.

Safety

CAUTION: Nitric acid and sulfuric acid can cause severe burns. Nitro compounds are toxic. Gloves should be worn throughout this experiment. Chloroform and methyl sulfoxide are both toxic and must be handled in the hood.

Nitration of Unknowns A and B

A solution of the unknown (0.500 g) in 3 mL of concentrated sulfuric acid contained in a 25-mL Erlenmeyer flask was cooled in an ice bath to 5 °C. Ice-cold concentrated nitric acid (1.1 mL) was added dropwise with a Pasteur pipet while maintaining the internal temperature at less than 8 °C. After each addition the flask was gently swirled. The entire addition took 20 min. After allowing the flask to stand in the ice bath for another 10 min, the resulting yellow solution was poured onto 10 g of crushed ice in a 50-mL beaker and stirred vigorously with a glass rod. The solid formed was collected by suction filtration and washed with cold water until the filtrate was neutral to litmus. The solid was placed in a vial, triturated with 1 mL of cold methanol, and again collected by suction filtration using a Hirsch funnel. The crystals were

allowed to remain under suction for 5 min and then pressed dry between the folds of a filter paper and used for NMR analysis. Typical yields were 0.40 g.² The product (approximately 100 mg) was dissolved in 0.7 mL of the appropriate solvent for obtaining the NMR spectra.

¹H NMR (DMSO), product of nitration of unknown A:³ δ 7.77 (br s, 2H, NH₂), 8.38 (br s, 3H, ring protons), 8.71 (br s, 1H, ring proton); ¹³C NMR (DMSO): δ 122.9, 126.6, 130.8, 134.6, 136.5, 148.6, 166.7.

¹H NMR (CDCl₃), product of nitration of unknown B: δ 3.92 (s, 3H, OCH₃), d 7.60 (t, 1H), 8.31 (m, 2H), 8.74 (t, 1H); ¹³C NMR (CDCl₃): δ 52.8, 124.5, 127.4, 129.7, 131.8, 135.3, 148.2, 164.9.

Nitration of Unknowns C and D

The same procedure as for unknowns A and B was followed with the following modification. The unknown solution was cooled to -8 °C in a salt-ice bath⁴ and ice-cold nitric acid was added dropwise while maintaining the internal temperature at less than 0 °C. After the addition was complete, the mixture was allowed to stand at less than 0 °C for 10 min.

¹H NMR (CDCl₃), product of nitration of unknown C: δ 2.7 (s, 3H, COCH₃), 7.67 (app t, 1H), 8.27 (1H, m), 8.39 (1H, m), 9.73 (m, 1H); ¹³C NMR (CDCl₃): δ 26.4, 123.4, 127.6, 130.2, 134.0, 138.5, 148.8, 196.2.

¹H NMR (CDCl₃), product of nitration of unknown D: δ 7.74 (m, 1H), 8.00 (m, 1H), 8.48 (m, 2H); ¹³C NMR (CDCl₃): δ 114.2 (CN), 116.6, 127.3, 127.6, 130.8, 137.7, 148.3.

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Notes

1. Unknowns A, B, C, and D are benzamide, methyl benzoate, acetophenone, and benzonitrile, respectively.

2. The average melting points (data obtained from 10 runs of each unknown) of the crude materials obtained from nitration of the unknowns (after allowing to air dry for a week) were unknown A, 138–141 °C (lit. 140 °C [5]); unknown B, 76–79 °C (lit. 78 °C [5]); unknown C, 77–79 °C (lit. 81 °C [5]); unknown D, 113–115 °C (lit. 118 °C [5]).

3. 3-Nitrobenzamide is not sufficiently soluble in CDCl₃. Hence, the spectra were recorded in *d*-6-DMSO.

4. If the temperature was allowed to rise much above 3 °C, a precipitous drop in yield was observed.

Literature Cited

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