Learning H-Coupled ^{13}C NMR in the First Month of Sophomore Organic Lecture
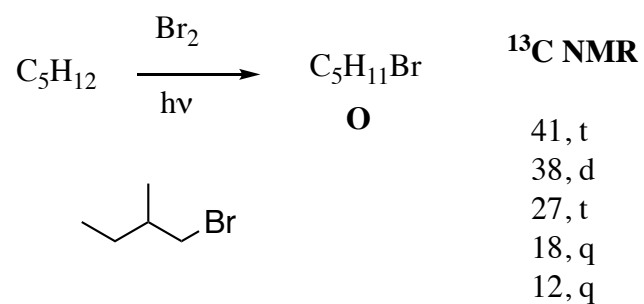
COMMUNICATION

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Abstract:

$$C_5H_{12} \xrightarrow[h\nu]{Br_2} C_5H_{11}Br$$

O

Br

^{13}C NMR

41, t
38, d
27, t
18, q
12, q

Using ^{13}C NMR data that includes ^{1}H coupling allows sophomore organic students to solve simple structural problems, even early in the first semester of the sophomore organic course.

Key Words: Second-Year Undergraduate, Organic Chemistry, Inquiry Based/Discovery Learning, Covalent Bonding

Learning ^{13}C NMR in the First Month of Sophomore Organic Lecture

One objective of sophomore organic chemistry is to enable each student to construct their

knowledge of organic structures. The efficacy of the guided inquiry/problem-based learning

approach to instruction in organic chemistry has been well documented, particularly in the

laboratory course.[1-9] Incorporating guided inquiry into the sophomore organic lecture course[10-12]

has been more challenging, especially early in the course. It is particularly dificult to formulate

questions for the first hour exam that test the developing reasoning of the student. A way to

approach this is to include ^{13}C NMR early in the course, with appropriate in class and homework

problems to give the student the opportunity to practice.

While there has been much discussion[13-26] of the use of ^{13}C NMR in the sophomore organic

course – Chamberlain[23] in particular nicely summarized the reasons to teach ^{13}C NMR before ^{1}H

NMR - this has mostly focused on the *laboratory* portion of the course, or on advanced[27-35]

coursework. Instruction in elementary ^{13}C NMR from the beginning of the *lecture* course can

equip the student with the tools necessary to solve simple structural problems.

Usually, ^{13}C NMR spectra are recorded without the coupling of the attached H atoms. If this

were not so, a methyl group would appear as a quartet, a methylene as a triplet, a methine as a

doublet and a carbon with no attached hydrogen atoms as a singlet. This offers a convenient

shorthand for communicating to a student (Fig. 1) the number of hydrogens attached to a

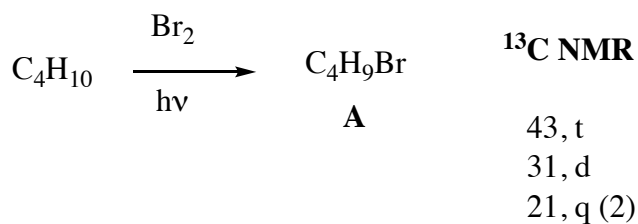particular carbon in a digital summary of the ^{13}C spectrum.

$$C_4H_{10} \xrightarrow[h\nu]{Br_2} C_4H_9Br$$

A

^{13}C NMR

43, t
31, d
21, q (2)

Figure 1. A first exam first semester ^{13}C NMR problem.

Often, the first reaction taught in the first semester of sophomore organic chemistry is free radical halogenation. This, then, can be the basis for a question on the first exam of the semester, as illustrated (Fig. 1).

The butane starting material (Fig. 2) could be either linear, *n*-butane **1**, leading to **B** or **C**, or branched, 2-methylpropane (*iso*-butane) **2**, leading to **D** or **E**. Since there two identical methyl groups in the product, the starting material must have been branched. The student can then deduce that product **A** has structure **D**, and write the mechanism.

Once the students have engaged with this reasoning process, it is useful to point out that one can deduce branching in an unknown structure. A methine (doublet in the ^{13}C spectrum) is a branch point, and a fully substituted carbon (singlet in the ^{13}C spectrum) is a double branch point. An unknown with no branching must be linear.

In parallel reasoning, an unknown with no branching will have two end groups. A methyl is an end group, as is a –Br. If there is a single branch, the student should be able to discern three end groups. If there are two branch points or a double branch point, there should be four end groups. In the example of Fig. 1, there are three end groups, two methyls, and a –Br.
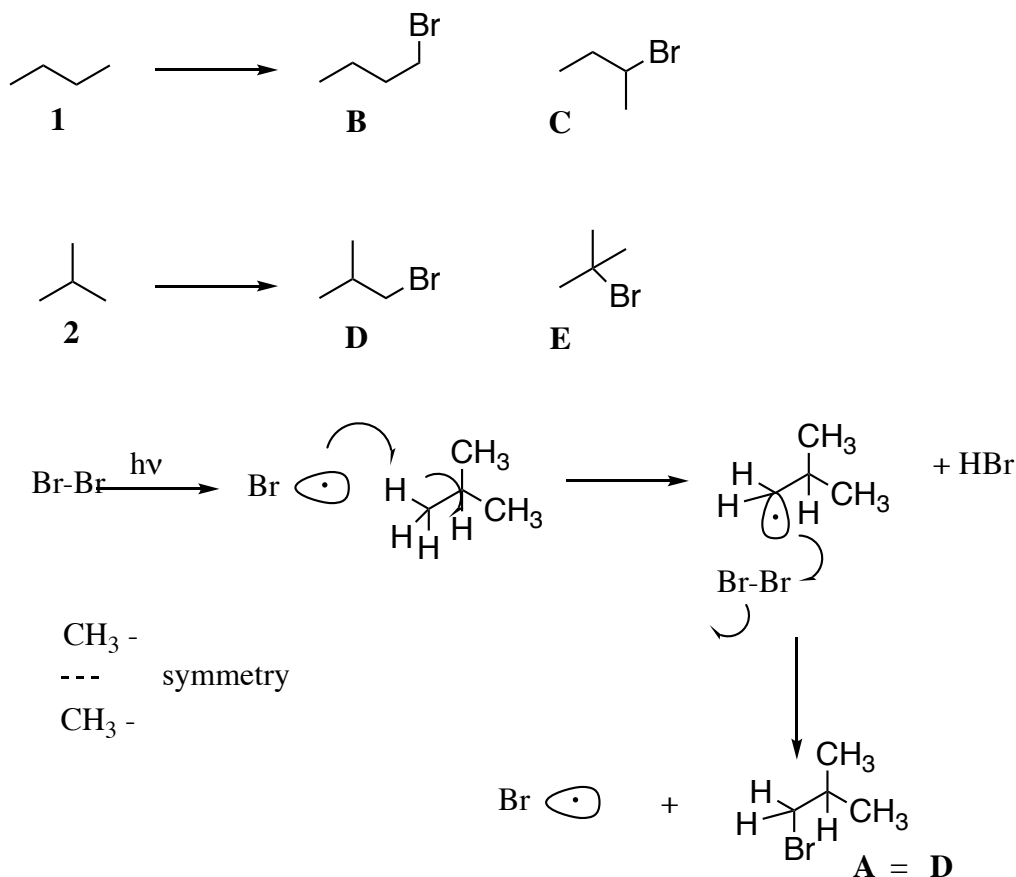
Figure 2. The solution to the problem in Figure 1.

Symmetry is also important. In the example of Fig. 1, the two methyl groups are the same. Since there is no other symmetry in the molecule, these must be attached to the same carbon.

The students can also note that there is one carbon with a larger chemical shift than the others. A reasonable hypothesis[15,23,36] is that this is the carbon where the bromine is attached, since that is the only methylene (CH_2) in the product.

$$C_5H_{12} \xrightarrow[h\nu]{Br_2} \underset{\textbf{F}}{C_5H_{11}Br}$$

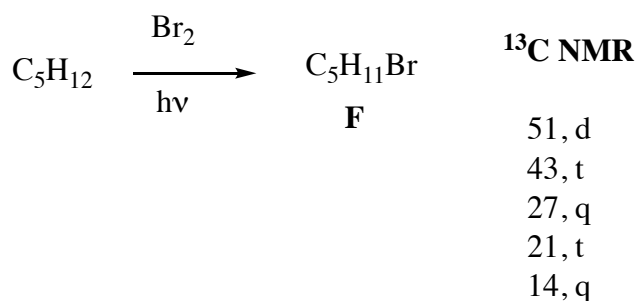**^{13}C NMR**

51, d
43, t
27, q
21, t
14, q

Figure 3. Another first exam first semester ^{13}C NMR problem.

The example in Fig. 3 is another such question from a first semester first exam. With five

carbons in the starting material, the analysis becomes more complex. Applying the same

reasoning as above, the starting material (Fig. 4) could be *n*-pentane **3**, leading to **G – I**, 2-

methylbutane **4**, leading to **J – M**, or 2,2-dimethylpropane **5**, leading to **N**. Since there is no

symmetry in the product, **F** (Fig. 3) could not be **I** or **K-N**. Further, the product **F** has two

methyl groups, limiting the possibilities to **H** or **J**. Since the carbon with the largest chemical

shift, with the –Br attached, has only one H, the product **F** must be **H**. The mechanism would the

same as Fig. 2.

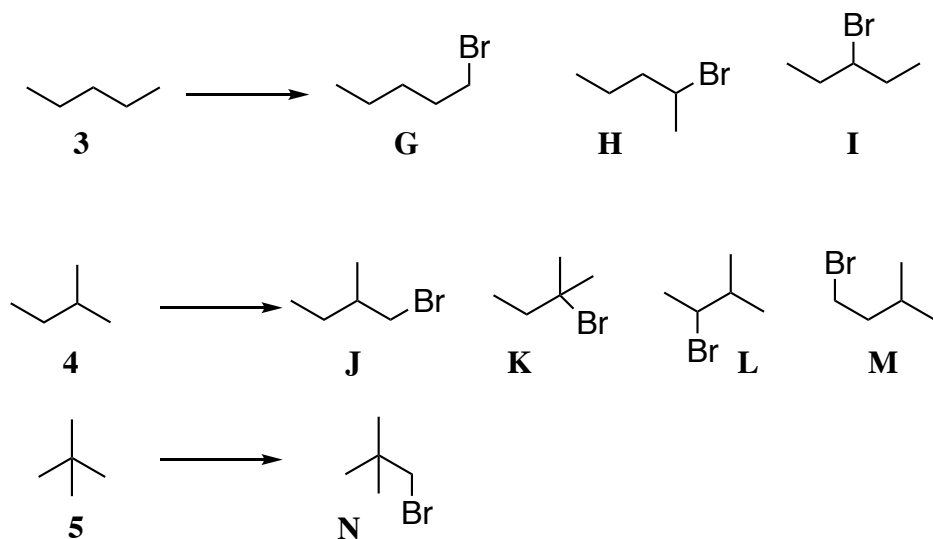**Figure 4.** Bromination products from pentane.

6

Each of the pentane-derived products **G**-**N** can be readily differentiated by ^{13}C NMR, as illustrated by a third example drawn from a first semester first exam (Fig. 5). Following the reasoning above, with two methyl groups and no symmetry, and –Br attached to a carbon with two H's, this must be **J**.

$$C_5H_{12} \xrightarrow[h\nu]{Br_2} C_5H_{11}Br$$

O

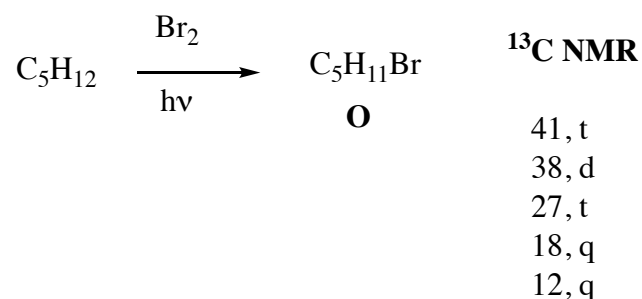**^{13}C NMR**

41, t
38, d
27, t
18, q
12, q

Figure 5. An additional first exam first semester ^{13}C NMR problem.

 Note that in these problems, there is no discussion as to *why* a particular product is formed. In the lecture, it was stressed that free radical bromination leads to a mixture of products.

The problems depicted here were each used in the first exam of a first semester sophomore organic course. Over those three years, with a mean enrollment of 119 students, consistently more than 100 students correctly deduced the product and drew out the mechanism correctly.

At the discretion of the instructor, more involved ^{13}C problems can be incorporated in exams as the course continues. The ^{13}C spectra of many simple organic molecules are readily available[37] online.

Note that in these problems the spectra are presented in digital format, for the convenience of the students. We have found that students have no difficulty transitioning to the more typical analogue format when they begin recording their own spectra.

Conclusion: Incorporating ^{13}C NMR early in the sophomore organic lecture course gives the student a way to reason about structural organic chemistry. Many additional problems with their answers, over a wide range of difficulty, are available at

http://www1.udel.edu/chem/valhalla/C331.html, http://www1.udel.edu/chem/valhalla/C332.html and http://www1.udel.edu/chem/valhalla/C333.html.

Associated Content

None

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Notes

Douglass F. Taber is the author of *Organic Spectroscopic Structure Determination: A Problem-Based Learning Approach* (Oxford University Press).

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TOC Graphic

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^{13}C NMR

O

41, t
38, d
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18, q
12, q