CHEM 347 – Organic Chemistry II – Spring 2015

Instructor: Paul Bracher

Quiz #2

Due: Monday, February 9th, 2015

2:00 p.m. (in class or Monsanto Hall 103)

| Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

- Please write your answers on the official answer sheet. No answers marked in this book-let will be graded. You must submit a hard copy of your answer sheet. Answer sheets submitted electronically will not be graded.

- You may use any resources you wish and collaborate with others.

- Any questions should be posted to the Black-board discussion board so all students have equal access to the information.

- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		30
II		20
III		12
IV		19
V		19
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.
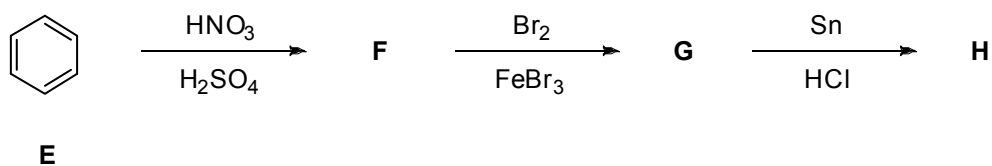
(1) _____C_____ Which of the following compounds would you expect to undergo the fastest heterolytic cleavage of its C–Br bond?
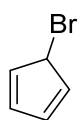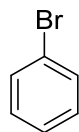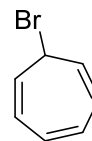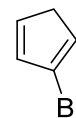
A   B   C   D

(a) compound **A**
(b) compound **B**
(c) compound **C**
(d) compound **D**
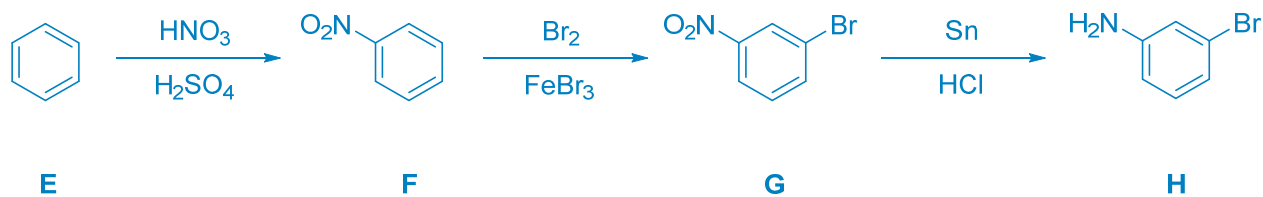(e) the rates for all four compounds will be exactly the same

Heterolytic cleavage means that the C–Br bond will break such that one atom gets both electrons (and the other atom gets none). It is generally more favorable for the Br atom to get both electrons since it is more electronegative than carbon. The loss of Br¯ from **B** or **D** will generate relatively unstable sp^2-hybridized carbanions. These carbanions are not stabilized by resonance delocalization; although you might think you can push electrons around, the orbital of the anion is orthogonal to the neighboring π system. Loss of Br¯ from **A** will generate an antiaromatic ring (4 π electrons). Loss of Br¯ from **C** will generate the aromatic—and hence, relatively stable—tropylium cation. So, heterolytic cleavage of the C–Br bond in **C** will occur fastest as it is the process that generates the most stable carbocation.

(2) _____B_____   What is the name of the major product (**H**) expected of the following sequence of reactions?

$$\text{E} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{F} \xrightarrow[\text{FeBr}_3]{\text{Br}_2} \text{G} \xrightarrow[\text{HCl}]{\text{Sn}} \text{H}$$

E

(a) 2-bromoaniline
(b) *m*-bromoaniline
(c) 3-chloroaniline
(d) 1-bromo-3-chlorobenzene
(e) 3-bromo-1-chlorobenzene

The expected sequence of reactions is:
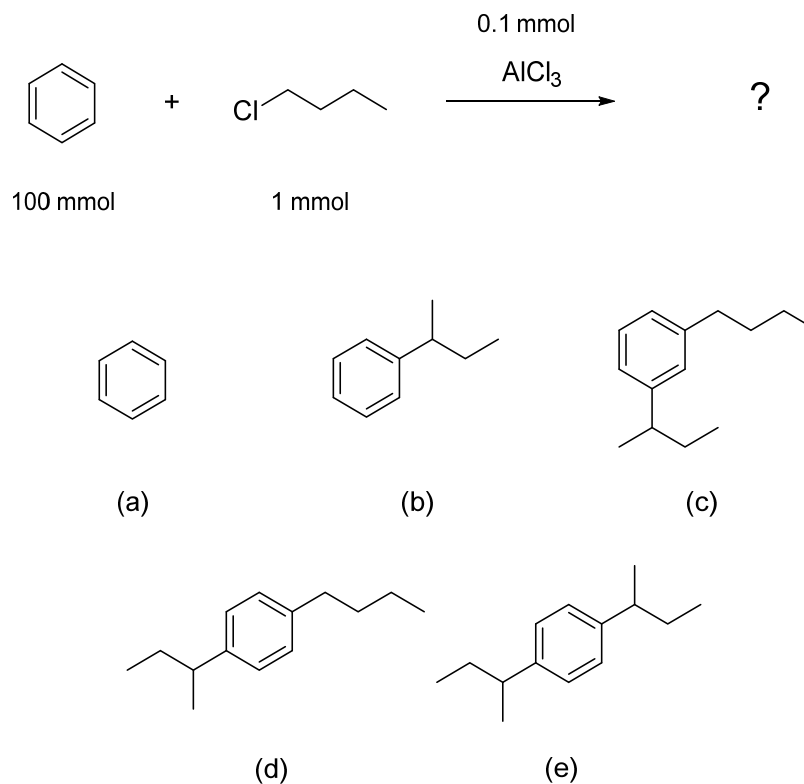
$$\text{E} \xrightarrow[\text{H}_2\text{SO}_4]{\text{HNO}_3} \text{F} \xrightarrow[\text{FeBr}_3]{\text{Br}_2} \text{G} \xrightarrow[\text{HCl}]{\text{Sn}} \text{H}$$

E   **F**   **G**   **H**

Compound **H** is named *meta*-bromoaniline or *m*-bromoaniline, for short. It is also named 3-bromoaniline.

(3)   _____C_____   Which of the following compounds would you expect to find in the <u>lowest</u> concentration when excess benzene is treated with 1-chlorobutane and aluminum trichloride?

0.1 mmol

$AlCl_3$

100 mmol   1 mmol

+   Cl~~~~

?

(a)   (b)   (c)

(d)   (e)

Product (c) is especially unlikely to form. In Friedel–Crafts alkylation reactions, primary alkyl halides often generate secondary or tertiary carbocations (following complexation with $AlCl_3$ and rearrangement). In this case, it is more likely for the ring to be alkylated as a *sec*-butyl group rather than an *n*-butyl group. Furthermore, once one alkyl group has added, the next addition will be preferentially directed to an *ortho* or *para* position. In product (c), the two alkyl groups have a *meta* relationship, and one of them is *n*-butyl.

(4)   _____D_____   Which of the following statements is not correct regarding compound **J**?
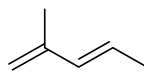
J

(a) compound **J** is named (3*E*)-2-methyl-1,3-pentadiene
(b) compound **J** has a less negative heat of hydrogenation than
2-methyl-1,4-pentadiene
(c) compound **J** has one other diastereomer
(d) compound **J** is incapable of participating in Diels–Alder reactions
(e) for the addition of HBr to **J**, the yield of 4-bromo-2-methyl-2-pentene
relative to 4-bromo-4-methyl-2-pentene will tend to increase with
increasing temperature

The best approach to these types of questions is to evaluate each choice. For (a), the name given is indeed correct. For (b), we are asked to compare the heats of hydrogenation of:


J
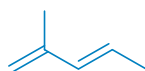
(3*E*)-2-methyl-1,3-pentadiene   2-methyl-1,4-pentadiene
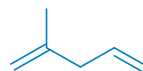
(conjugated π bonds)   (non-conjugated π bonds)

While both compounds have two π bonds and are hydrogenated to the same final product, compound **J** will have a less negative heat of hydrogenation than the compound on the right because the π bonds in **J** are conjugated (with an uninterrupted line of *sp*^{2} carbons). This electronic structure imparts additional stability to **J**, meaning less heat will be released upon hydrogenation of both compounds.

For (c), compound **J** does indeed have one other diastereomer: (3Z)-2-methyl-1,3-pentadiene:

J
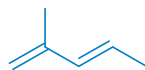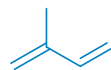
(3*E*)-2-methyl-1,3-pentadiene   (3*Z*)-2-methyl-1,3-pentadiene

For (d), we finally find an incorrect statement, as compound **J** is capable of acting as a diene in the Diels–Alder reaction. While compound **J** is drawn in an *s-trans* conformation, it is easily capable of rotating into the *s-cis* conformation required for the reaction.

   For (e), 4-bromo-2-methyl-2-pentene is a thermodynamic product (more-stable alkene, result of 1,4-addition) while 4-bromo-4-methyl-2-pentene is a kinetic product (less-stable alkene, result of 1,2-addition) of the addition of HBr. As a result, we expect the yield of the former to improve relative to the latter as the temperature of the reaction increases.

J

a thermodynamic product   a kinetic product from
from 1,4-addition of HBr   1,2-addition of HBr

         Br   Br

4-bromo-2-methyl-2-pentene   4-bromo-4-methyl-2-pentene
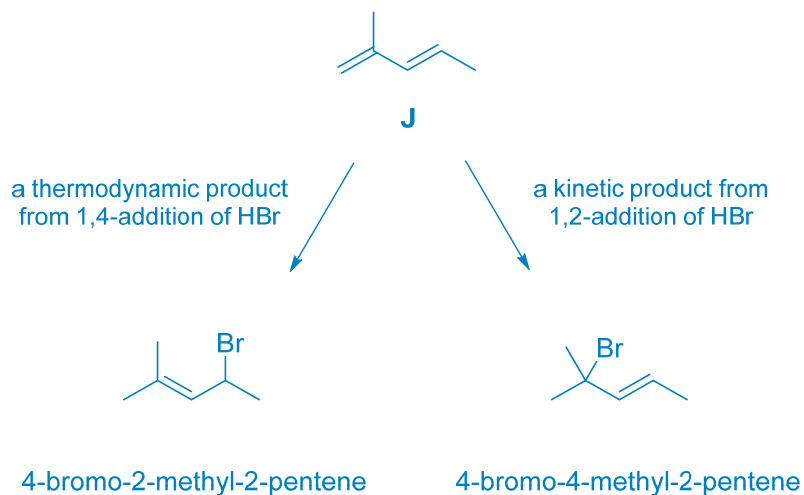
(5)   _____E_____   Which of the following steps would be the <u>least</u> reasonable to include when drawing a mechanism for the formation of **L** from **K** in the reaction below?

**K** → (Br₂ / ROOR) → **L**

(a)

(b)

(c)

(d)

(e)
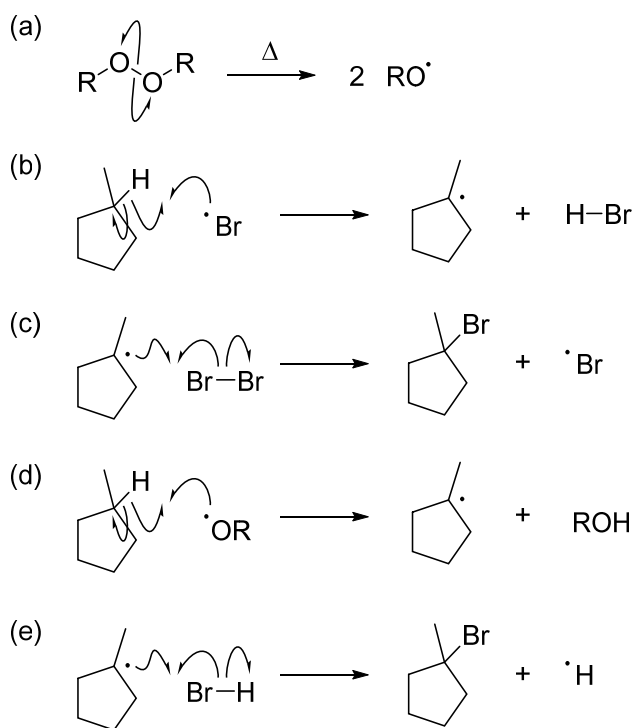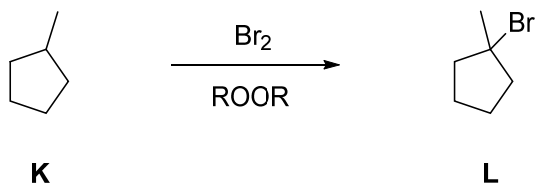
Steps (a) through (d) are all found in the standard mechanism for this radical reaction. Step (e) is not a standard propagation step because it is quite endothermic relative to the alternative propagation step (c), which is exothermic.

(6)   <u>D</u>   Which of the following reactions is <u>not</u> fatally flawed and will proceed as drawn?
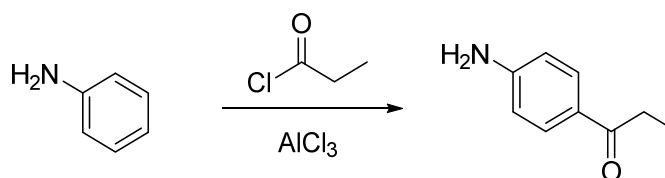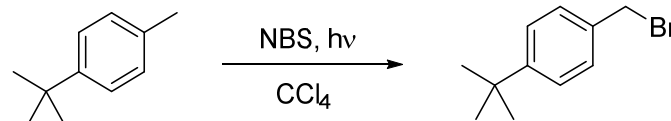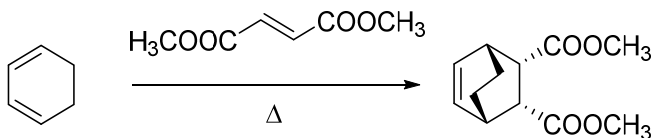
(a)

NBS, hν / PhCH₃

(b)

AlCl₃

(c)

AlCl₃

(d)

NBS, hν / CCl₄

(e)

Δ
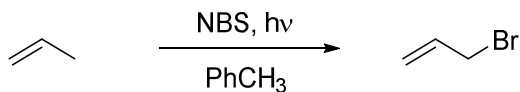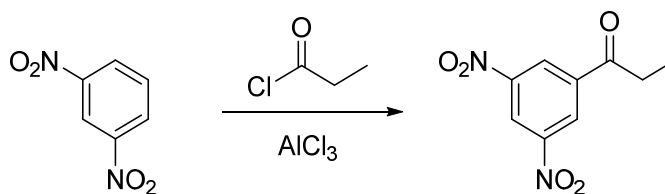
Only reaction (d) will proceed as drawn. In reaction (a), the NBS will preferentially react with the PhCH₃ solvent over the 1-propene. In reaction (b), the ring is too deactivated to undergo Friedel–Crafts acylation. Remember, nitrobenzene itself is too deactivated to undergo either Friedel–Crafts acylation or alkylation. In reaction (c), the nitrogen will complex with and poison the AlCl₃ catalyst. This complexation also deactivates the ring. In reaction (e), the ester groups will be *trans* on the new cyclohexene ring since they were *trans* on the dieneophile and stereochemistry is retained in concerted reactions like the Diels–Alder.

Problem II. Mechanism (20 points).

(i) (14 points) Draw sensible mechanisms for the formation of **N** and **P** when **M** is treated with bromine. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all significant resonance forms that account for the stability of the intermediates in the reactions.
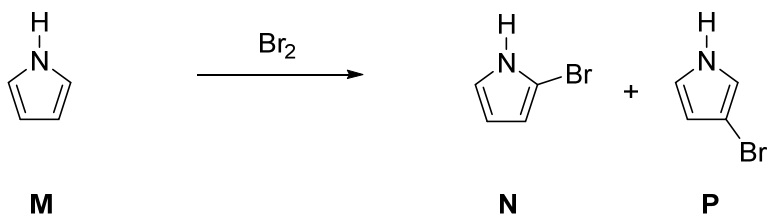

(one more resonance structure for this intermediate)
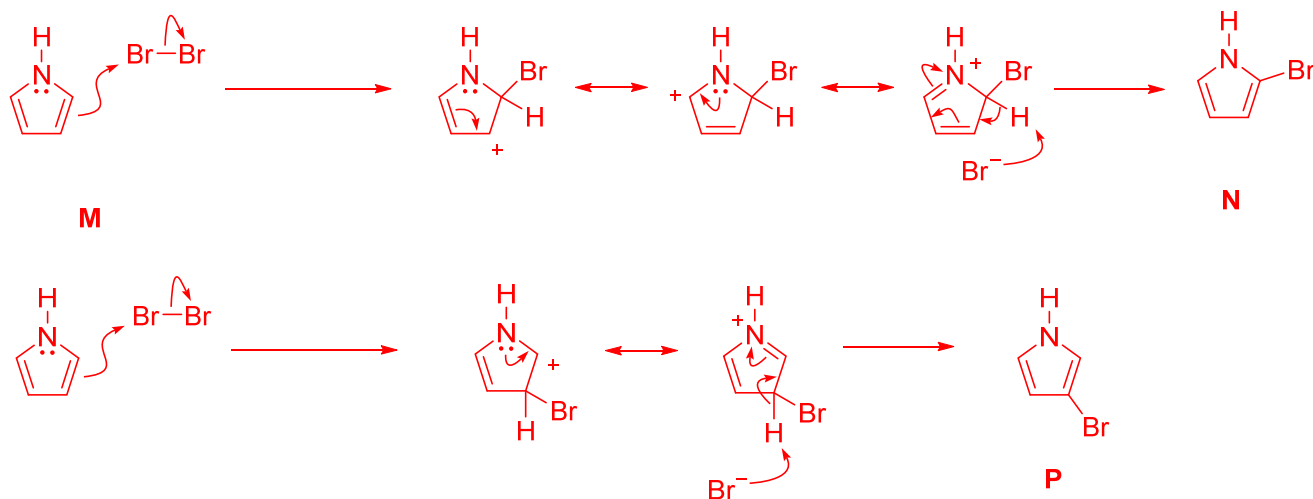
(ii) (6 points) Based on your proposed mechanisms, do you expect **N** or **P** to be produced in higher yield? Write your choice in the box on your answer sheet and briefly explain the reason behind your selection.

Compound **N** should be produced in higher yield because the mechanism corresponding to its formation proceeds via an intermediate that is more stable—it has an extra resonance form—than the intermediate for **P**. Recall, the Hammond Postulate says that the relative speed of competing endothermic steps typically depends on the relative stability of the product (here, the carbocation intermediate).

Problem III. Explanation (12 points). Compound **Q** has a remarkably large dipole moment for a hydrocarbon. Provide a brief explanation for this observation using words and structures. The dipole moments of **R** and **S** are provided as a reference for values more typical of hydrocarbons; you do not need to include these compounds in your explanation.
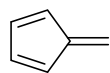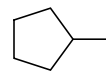
Q	**R**	**S**
$\mu = 1.20$ D	$\mu = 0.42$ D	$\mu < 0.5$ D

Pushing the electron pair from the exocyclic π bond in **Q** into a lone pair on the inner carbon makes the ring aromatic (conjugated with 6 π electrons). The extra stability associated with aromaticity makes this resonance form a greater contributor to the resonance hybrid than would otherwise be expected. As this second resonance form also has a higher separation of charge, the dipole moment of the molecule is correspondingly large.
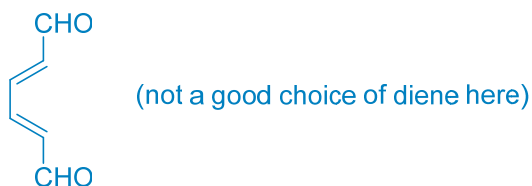
dipole moment
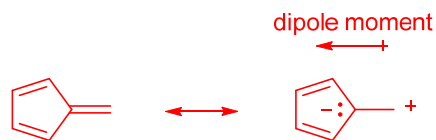
Q

$\mu = 1.20$ D

Problem IV. Synthesis (20 points). Provide a synthetic route—i.e, a sequence of reactions—to produce compound **U** from compound **T** and any reagents you need. Note: You need only account for the relative (not absolute) stereochemistry of the stereocenters. Basically, make sure the substituents on the ring have the in-dicated *cis*/*trans* relationships, not necessarily the indicated *R/S* relationships.

**T**　　　　　　　　　　　　　　　　　　　　　**U**

NaOCH₃ / CH₃OH

1. O₃
2. DMS

(+/–)
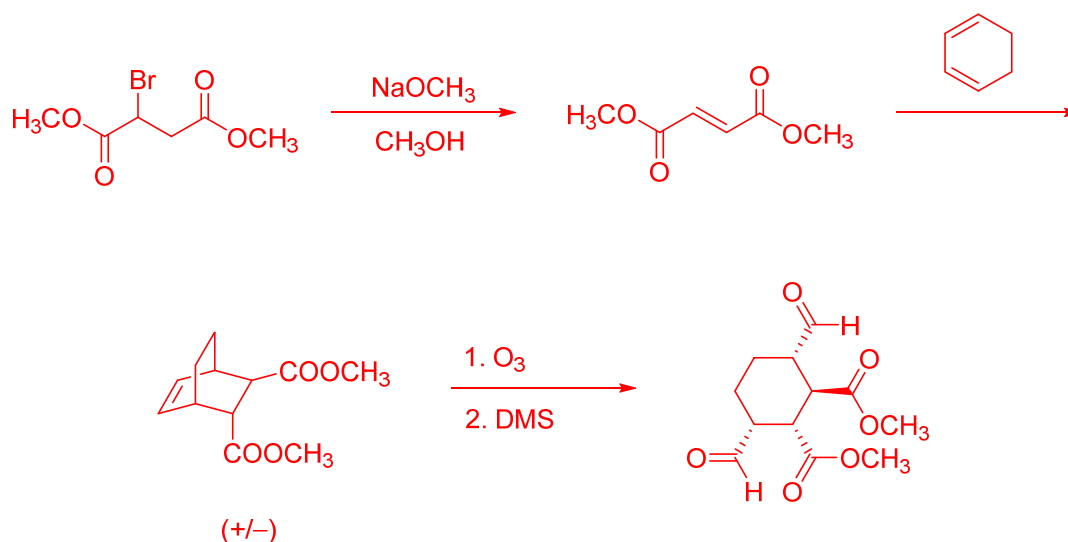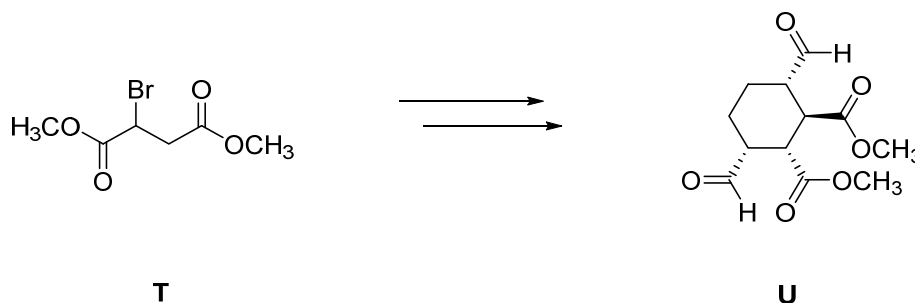
Approach

The new six-membered ring—and the fact that we covered the Diels–Alder reaction in this unit—screams that you should use the Diels–Alder reaction here. A common dieneophile can be generated by eliminating HBr from the starting material. The major product of this elimination will be the *trans* alkene, owing to the steric favorability of having the bulky groups farther away from each other. The rest of the problem is picking the right diene and realizing that one of the few ways you know to make aldehydes at this point is via ozonolysis.

Note that the following diene is a poor choice because Diels–Alder reactions typically fail when both the diene and dieneophile have electron-withdrawing groups. It is best when one (diene or dienephile) has elec-tron-donating groups and the other has electron-withdrawing groups.

CHO　　　(not a good choice of diene here)

CHO

Problem V. Synthesis (19 points). Provide a synthetic route—i.e, a sequence of reactions—to produce compound **Y** from ^{13}C-enriched benzene (**X**) and any other reagents you need. Assume that you do not want to waste any of **X** by using it in vast excess in any reaction.

(all ^{13}C atoms)

X

(+/−)

Y
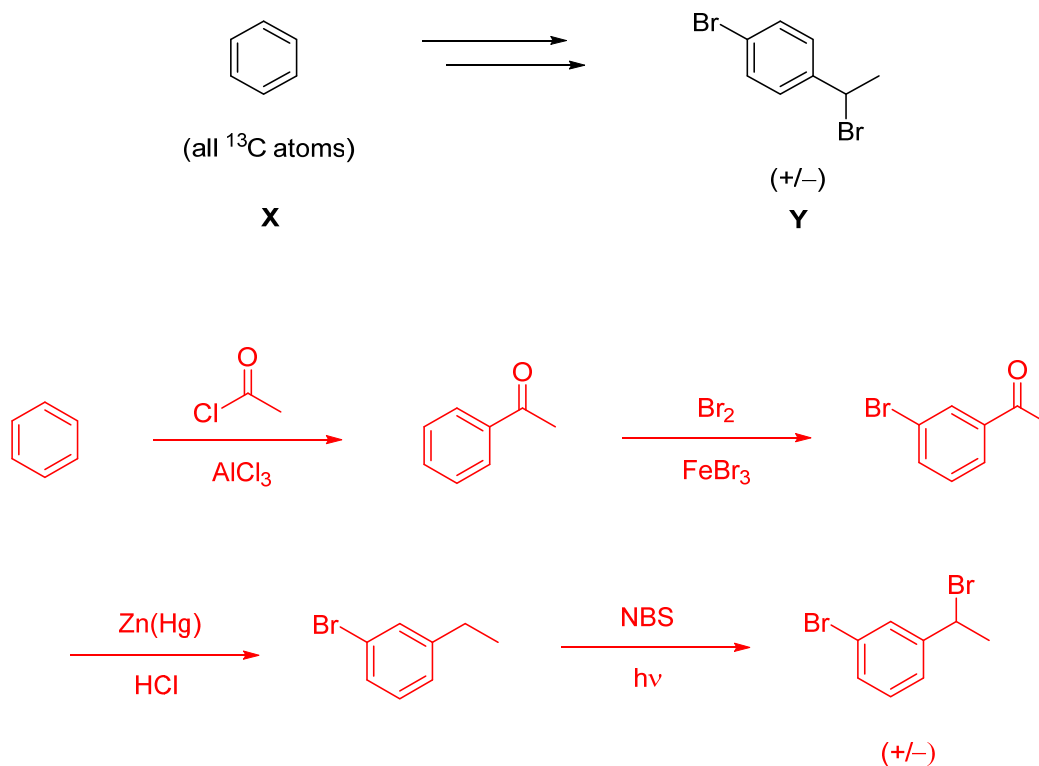
The only reason ^{13}C-enriched benzene (which is expensive) was chosen for this problem is so that you don't waste it by running something like a Friedel–Crafts alkylation, where you might have used it in vast excess to avoid overalkylation. (Of course, in the 'real world', you might be able to get around this issue by recovering unreacted starting material.) So, you begin by Friedel–Crafts acylation to install the acetyl group (a *meta* director) and proceed from there.

And in all honesty regarding the bromination with Br$_2$/FeBr$_3$, I am not so sure that the second reaction won't install the bromine atom on the carbon that is α to the carbonyl group. It might be dicey. But since we have not covered this chemistry yet, let's go with the scheme written above.

Note that you must install the benzylic bromine atom in the last step lest one of the strong Lewis acid reagents remove it in a subsequent step.