Massachusetts Institute of Technology

5.46: Organic Structure Determination
Hour Exam 2

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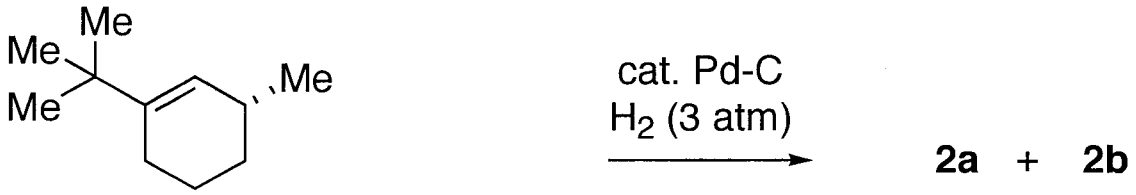
May 12, 2004

Your Name: _____

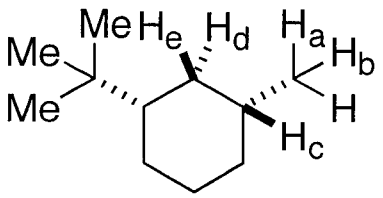
Instructions: You have **50 minutes** to complete this **closed book, closed notes** exam. There are 8 pages (including this page) and 5 pages of reference information. You may use a calculator, straight edge, and molecular model set, but no notes, books or other information are allowed. Please read through the entire exam before beginning. Where applicable, show your work to receive partial credit.

Question	Points Received/Possible
1.	_____ / 24
2.	_____ / 20
3.	_____ / 20
4.	_____ / 36
Total:	_____ / 100

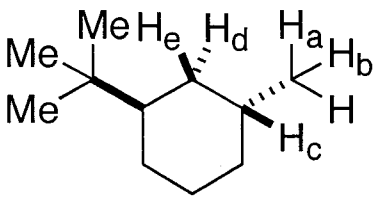
1. (24 points total) As indicated in the scheme below, a suspension of enantiomerically pure (>99% ee) *(R)*-1-*tert*-butyl-3-methylcyclohexene (**1**) and palladium on carbon (catalyst) was placed under an atmosphere of hydrogen gas (3 atm) until **1** was completely converted to two diastereomeric products, **2a** and **2b**. Below **each diastereomer shown, circle the number** corresponding to the predicted coupling constant (in Hz) of each pair of indicated protons that you would expect to see in a ^{1}H NMR spectrum in $CDCl_3$ at ambient room temperature.



(R)-1-*tert*-butyl-3-methylcyclohexene (**1**)



2a



2b

$J(H_a–H_b)$	0	1	3	7	10	15	20	27
$J(H_a–H_c)$	0	1	3	7	10	15	20	27
$J(H_a–H_d)$	0	1	3	7	10	15	20	27
$J(H_c–H_d)$	0	1	3	7	10	15	20	27
$J(H_c–H_e)$	0	1	3	7	10	15	20	27
$J(H_d–H_e)$	0	1	3	7	10	15	20	27

$J(H_a–H_b)$	0	1	3	7	10	15	20	27
$J(H_a–H_c)$	0	1	3	7	10	15	20	27
$J(H_a–H_d)$	0	1	3	7	10	15	20	27
$J(H_c–H_d)$	0	1	3	7	10	15	20	27
$J(H_c–H_e)$	0	1	3	7	10	15	20	27
$J(H_d–H_e)$	0	1	3	7	10	15	20	27

(20 points total)

2a. (17 points) A sample of 2-butanol of unknown enantiomeric excess (ee) was dissolved in pyridine and treated with the acid chloride of *(R)*-1-methoxy-1-trifluoromethylphenylacetic acid (*(R)*-MTPA chloride). A ^{1}H NMR spectrum of the product mixture showed two 3H doublets (13:7 ratio) and two 2H multiplets (13:7 ratio). The 3H doublet of the major diastereomer was *downfield* relative to the 3H doublet in the minor diastereomer, whereas the 2H multiplet of the major diastereomer was *upfield* relative to the 2H multiplet in the minor diastereomer.

In the boxes provided, **draw the structures** of the two enantiomers of 2-butanol and using the Cahn-Ingold-Prelog convention, **write the configuration** of each (*(R)* or *(S)*) next to each structure. Based on the information in the preceding paragraph, **clearly write "major"** next to the major enantiomer of the original 2-butanol sample, and **clearly write "minor"** next to the minor enantiomer. (Show your analysis that led to your conclusion on the **next page** if you would like consideration for partial credit.)

(Draw **one** of the 2-butanol enantiomers; write the configuration next to the stereogenic center, write **major** or **minor** next to the structure, as appropriate.)

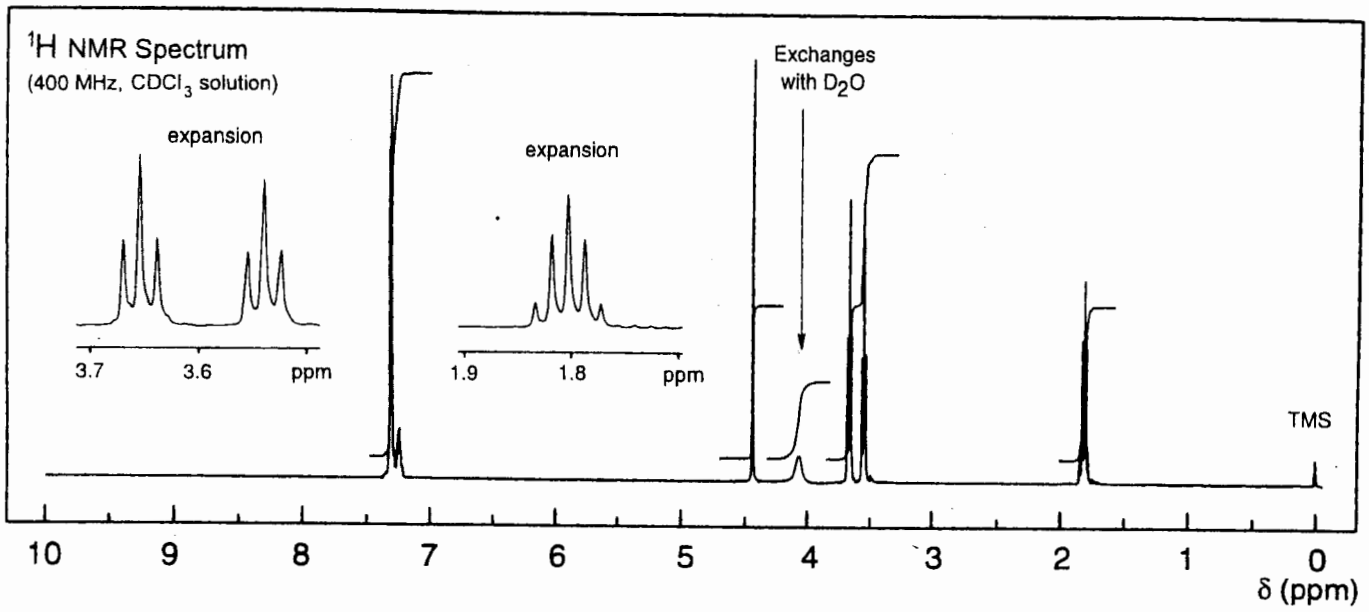
(Draw **the other** 2-butanol enantiomer;.) write the configuration next to the stereogenic center, write **major** or **minor** next to the structure, as appropriate.)

2b. (3 points) What is the ee of this sample of 2-butanol, expressed as a **percentage**? (Show your work **on the next page** if you would like consideration for partial credit.) Write your final answer neatly in the box provided.

(**Write the percent ee** of the sample of 2-butanol.)

2. (continued) **Show your work for problems 2a and 2b in the space provided below.**

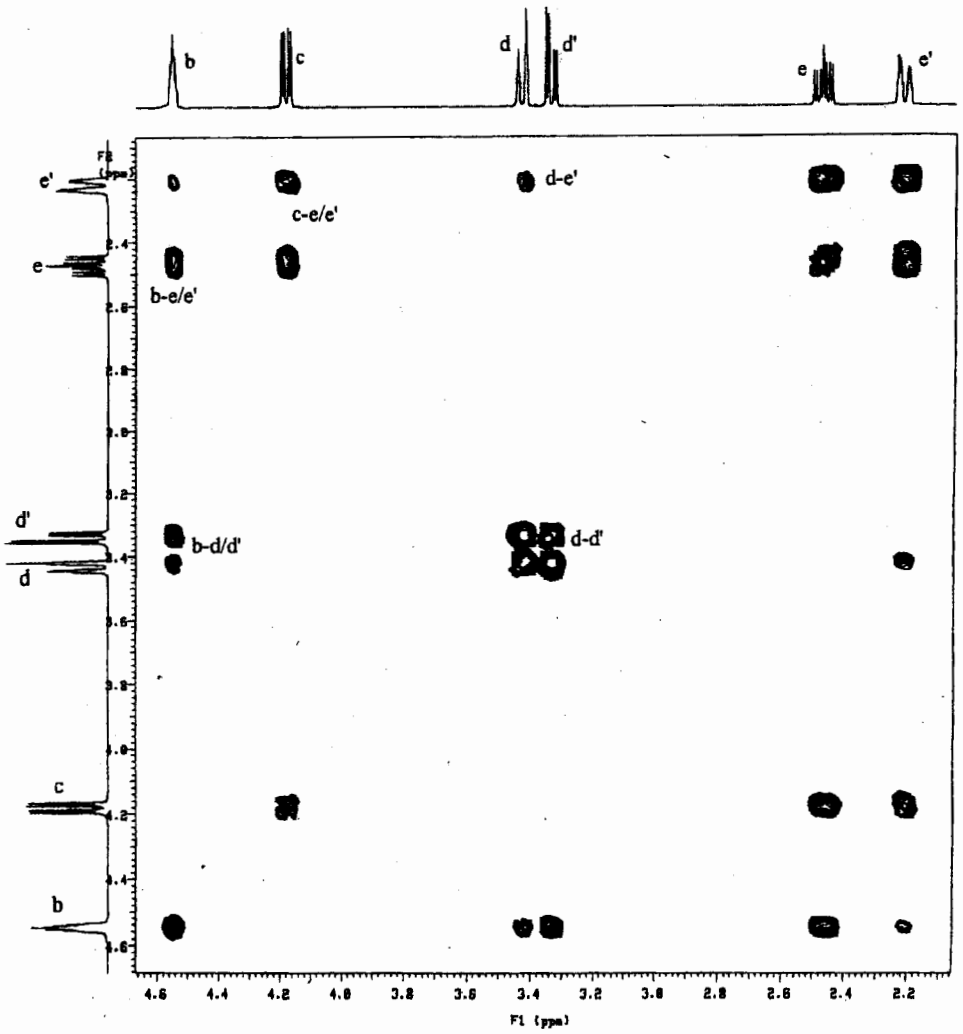
3. (20 points) In the box provided on the following page, **draw the structure** of the compound with molecular formula $C_{10}H_{14}O_2$ that satisfies data in the ^1H NMR spectrum provided. Explicitly show stereochemistry, double bond geometry, etc., if applicable.



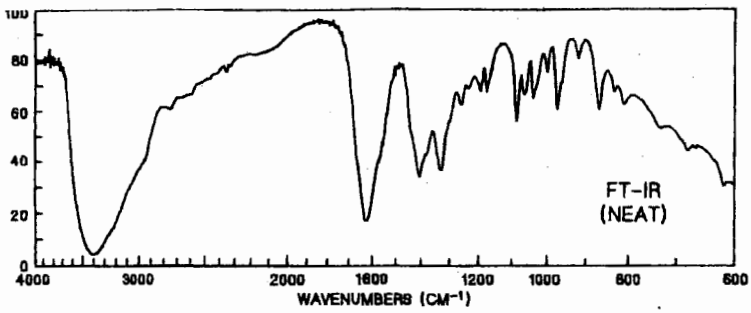
(**draw the structure** of the compound in this box.)

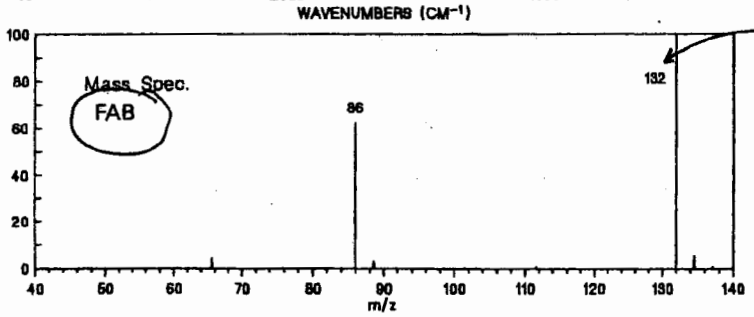
4. (36 points) In the box provided, **draw the structure** of the compound that satisfies the data provided below (^{1}H–^{1}H COSY spectrum) and on the next page. Note that the results of an nOe DIFF experiment are provided in the ^{1}H NMR. The letters above the peaks in the ^{13}C NMR spectrum refer to their multiplicity in a spectrum (not shown) acquired **without** broadband decoupling (S = singlet; D = doublet; T = triplet; Q = quartet). Explicitly show stereochemistry, double bond geometry, etc., if applicable. **On page 8, show your work** if you would like consideration for partial credit.

(**draw the structure** of the compound in this box.)



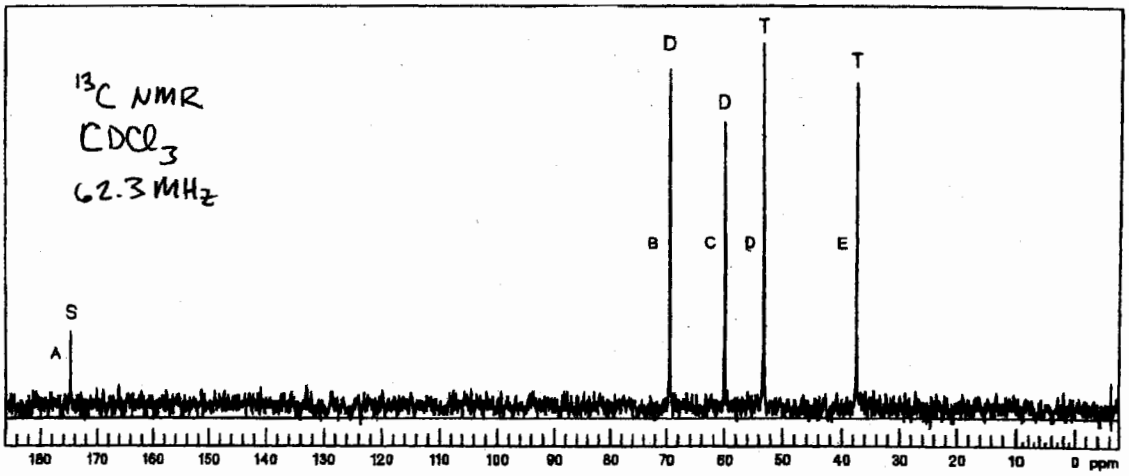
4. (continued) – IR, FAB-MS, and ^{13}C and ^{1}H NMR spectra for the unknown in problem 4.

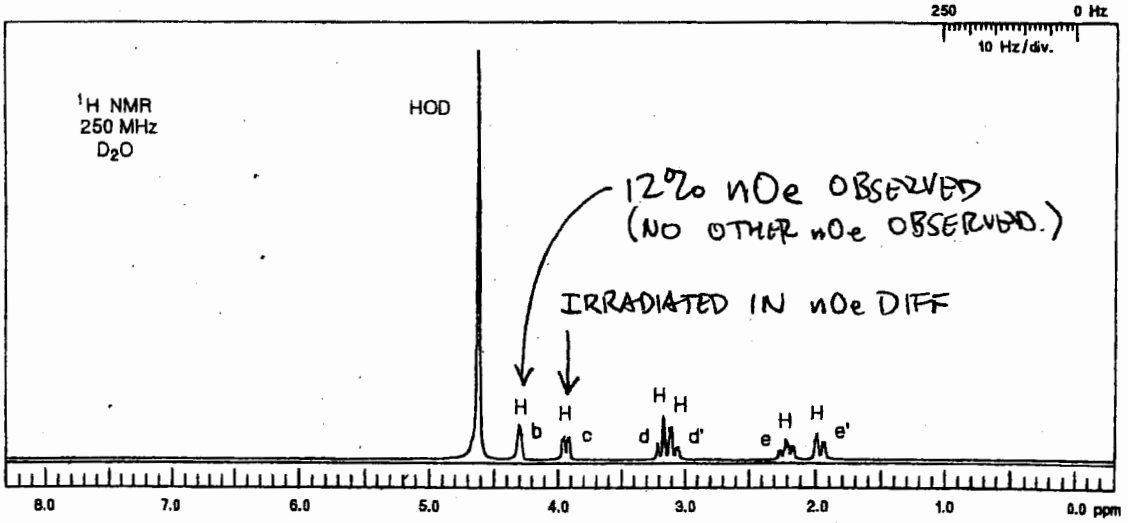




$(M+H)^+$

$MF = C_5H_9NO_3$





4. (continued) **Show your work for Problem 4 in the space below if you wish consideration for partial credit.**