Department of Chemistry and Biochemistry

Chemistry 59-230/232 **Midterm #1**

Time: 50 min. **Oct. 19, 2005**

NAME _____ **ID#** _____

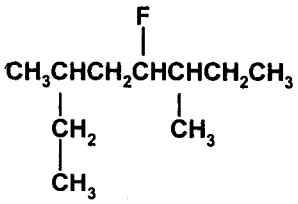
LAB SECTION *(If you can't remember, give your TA's names)*

_____

Note: ***Please answer on the test paper.*** *There is an extra sheet for rough work at the back, but it will not be marked. Tests written in pencil will be marked, but cannot be returned for remarking. For the 'promised' size ranking, see the intro to* ***5a****.*

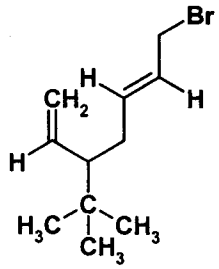
1. Give correct systematic names for the following compounds. Include stereochemical descriptors where relevant. (4 marks each, total 16 marks)

a



4 - FLUORO - 3,6 - DIMETHYLOCTANE

b.

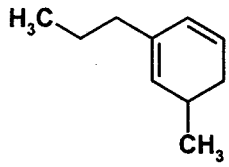


HEPTA-1,5-DIENE ALSO OK

trans OR (E) 7- BROMO - 3- DIMETHYLETHYL - 1,5-HEPTA DIENE

tert-BUTYL ALSO OK

c.

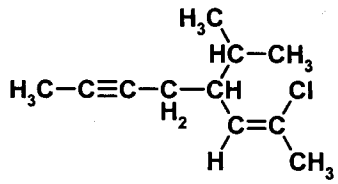


CYCLOHEXA-1,3-DIENE ALSO OK

6- METHYL - 2 - PROPYL - 1,3 - CYCLOHEXADIENE

STEREOCHEMICAL DESCRIPTOR IS NOT NEEDED - IF YOU PUT ONE IT IS, IT'S EITHER (1Z,3Z)- OR CIS,CIS-

d.



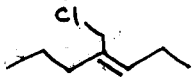
trans OR (Z) 2- CHLORO-4 - ISOPROPYL - 2-OCTEN -6 -YNE

OCT - 2-EN-6 -YNE ALSO OK

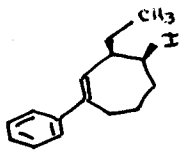
METHYETHYL ALSO OK

2. Draw structures which correspond to the following given names. Drawings showing only carbons and other non-hydrogen atoms are acceptable. Please include the appropriate stereochemical aspects of the structure where it is needed. (4 marks each, total 12)

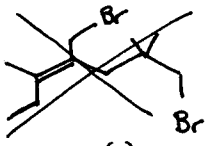
a. *trans*-4-chloromethyl-4-heptene - OH, HECK, THIS NAME IS WRONG - SHOULD BE NAMED AS A -3-HEPTENE



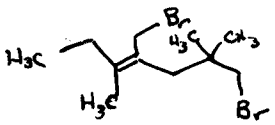
b. *cis*-3-ethyl-4-iodo-1-phenylcycloheptene (Note: I have *not* put a stereochemical descriptor in for the alkene stereochemistry)



c. (Z) 7-bromo-4-bromomethyl-3,6,6-trimethyl-3-heptene

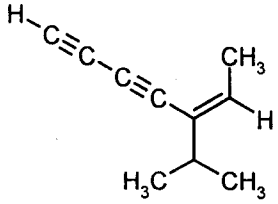


IS (E) ∴



3. (Total 15 marks)

a. Apply the *Z* or *E* stereochemical descriptor where relevant in the following molecule. Show how you arrived at the distinction. (5 marks)



LEFT CARBON — TOP C → C,C,C (TRIPLE BOND) ⇐ "WINS"

BOT C → C,C,H

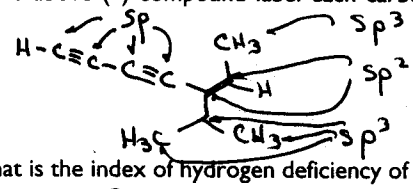
RIGHT CARBON — TOP C ⇒ WINS

BOT H

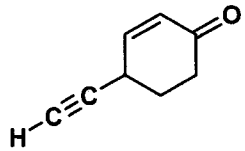
HIGHER PRIORITY GROUPS ON SAME SIDE

∴ (Z)-

b. In the above (^) compound label each carbon atom with the appropriate hybridization. (3 marks)



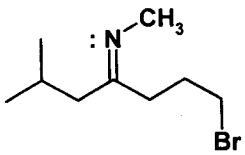
c. What is the index of hydrogen deficiency of the following compound? (2 marks)



1 RING ⇒ 1
2 C=X'S ⇒ 2
1 C≡C ⇒ 2

5

d. Not only C=C double bonds can have geometric isomers. Apply the *Z* or *E* stereochemical descriptor where relevant in the following molecule. Show how you arrived at the distinction. (5 marks) By the way, there are <u>two bonus marks</u> if you can name the double bonded functional group.



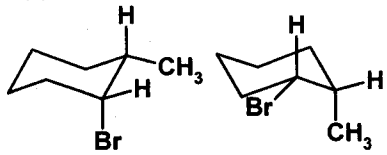
TOP ATOM ⟹ LEFT – LONE PAIR
RIGHT – C ⟹ WINS

BOT ATOM → LEFT C → C, H, H → C, C, H ⟹ WINS
RIGHT C → C, H, H → C, H, H
↑ TIE TIE

HIGHEST PRIORITY GROUPS "ACROSS" DOUBLE BOND
∴ (E)-

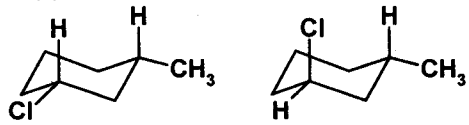
4. For each of the below, assign the appropriate terminology (structural isomers, stereoisomers, geometric isomers, different conformations of the same molecule, identical) to the following. (Total 6 marks)

a. (2)



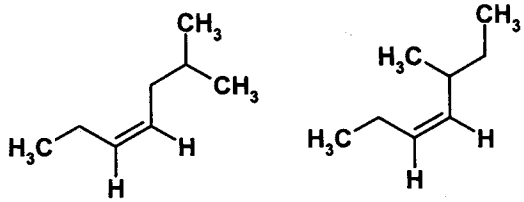
DIFFERENT CONFORMATIONS

b. (2)



STEREOISOMERS
- I WILL ACCEPT GEOMETRIC, BUT THIS IS NOT REALLY TRUE

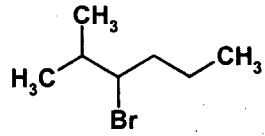
c. (2)

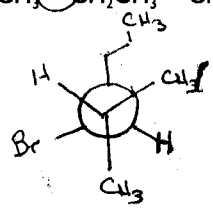


STRUCTURAL ISOMERS
(CONSTITUTIONAL IS OK, TOO)

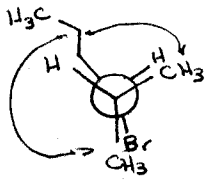
THAT'S AN EQUAL SIGN, NOT A C=C

5. a) (22 marks) Draw the Newman projections of the indicated compound in the most stable staggered conformation of the following compound, viewed down the C2-C3 bond. (In terms of size, $C(CH_3)_3 > CH(CH_3)_2 > CH_2CH_2CH_3 = CH_2CH_3 > CH_3 > NH_2 > OH > F, Cl, Br, I > \mathbf{H}$) (5 marks)





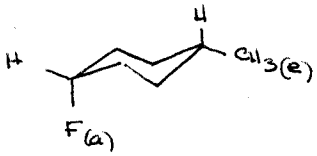
b) Draw the Newman projection of the same compound (as in 'a') in the most stable eclipsed conformation (again, down the C2-C3 bond). Give the name for the relative orientation of the propyl group on the back carbon with respect the methyl groups on the front carbon (6 marks).



ANTICLINAL (BOTH CH_3'S)

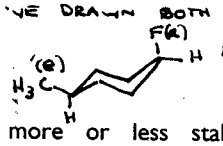
THE KEY HERE IS THAT THE BIGGEST GROUP (PROPYL) SHOULD BE EXACTLY LINED UP (SYNPERIPLANAR) WITH THE SMALLEST GROUP (HYDROGEN)

c) Draw *cis*-1-fluoro-4-methylcyclohexane in its most stable conformation. Label the non-hydrogen substituents as axial or equatorial (6 marks).



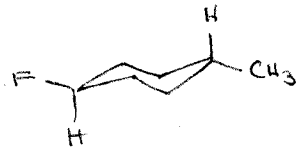
METHYL GROUP IS LARGER THAN FLUORINE
∴ IT 'WANTS' TO BE EQUATORIAL MORE THAN FLUORINE

I'VE DRAWN BOTH "DOWN", BUT BOTH "UP", AS IN



, IS ALSO FINE.

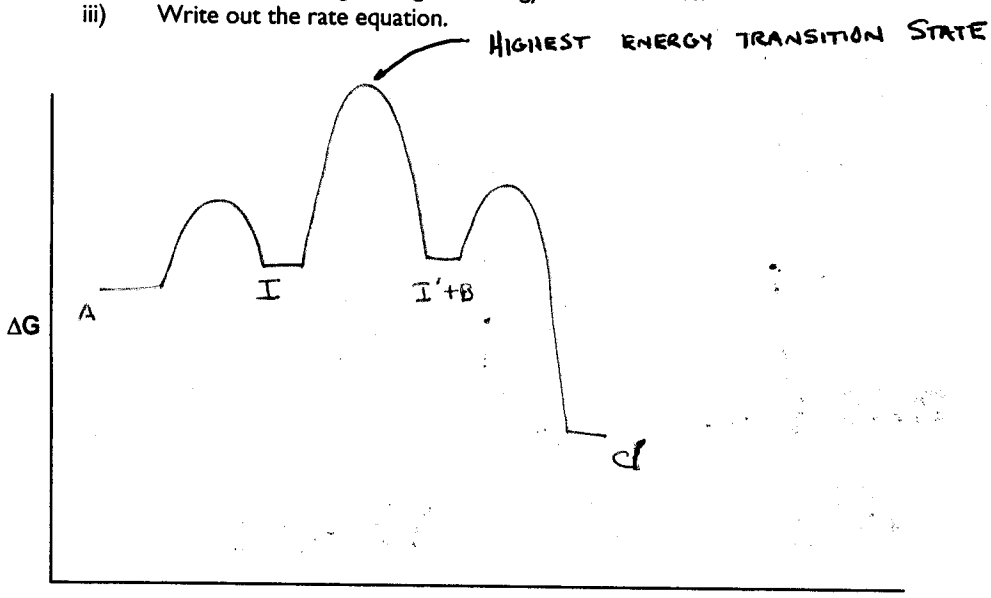
d) Is *trans*-1-fluoro-4-methylcyclohexane more or less stable than *cis*-1-fluoro-4-methylcyclohexane? Please rationalize your answer – by *either* words or drawn structures (5 marks).



BETTER (MORE STABLE) BECAUSE BOTH NON-HYDROGEN SUBSTITUENTS GET TO BE EQUATORIAL

6a. **(10 marks)** An exothermic reaction between A and B to give C occurs in three steps. A is consumed in the 1st step and B is consumed in the third step. The 2nd step is the rate determining one.

i) Draw the energy versus reaction coordination plot for this transformation.
ii) Indicate by labeling the highest energy transition state.
iii) Write out the rate equation.

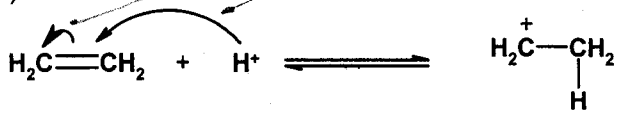


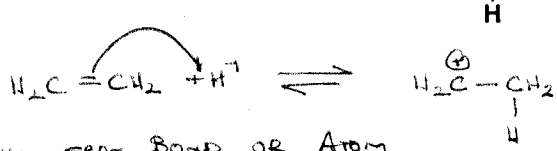
Rate v = k [A]

b. Which of the following are proper uses of the curved arrow, and which are not? (6 marks). For any incorrect ones, show what the arrows would indicate the product to be (no matter how unstable it looks).

i)

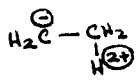
NO GOOD
NO GOOD } SHOWING MOVEMENT IN OPPOSITE DIRECTION TO ELECTRON FLOW



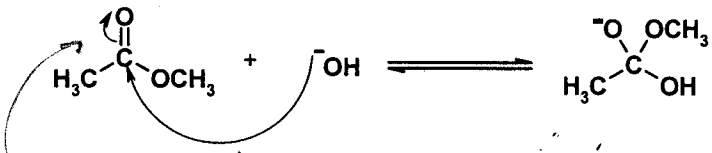


WOULD BE RIGHT FOR THE REACTION

CAN SHOW FROM BOND OR ATOM

WHAT THE ARROWS ACTUALLY FORM IS  , WHICH IS BONDING NONSENSE

ii)



VERY APPROPRIATE;

ALSO CORRECT

c) Rank the following in terms of acid strength, from strongest to weakest (3 marks).

H_2S NH_3 HI PH_3 HCl

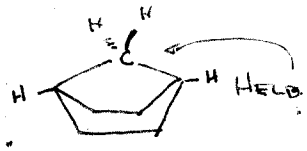
THAT'S AN "I"

HI > HCl > H_2S > PH_3 > NH_3

Bonus. (Up to 3 additional marks) Six membered all carbon ring systems can occasionally prefer to exist in a boat conformation. Can you supply a reasonable example?

THE BEST TYPE OF ANSWER IS....

=



HELD IN BOAT BY BOND