Seat No. _____ Name KEY

(Please print your name and **CIRCLE** your last name)

CHEMISTRY 331

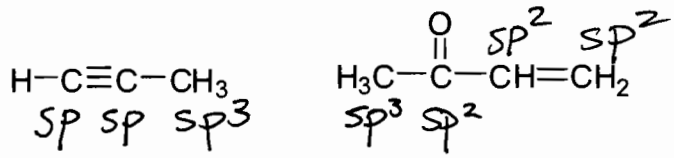
FINAL EXAM

Friday, May 9, 2008

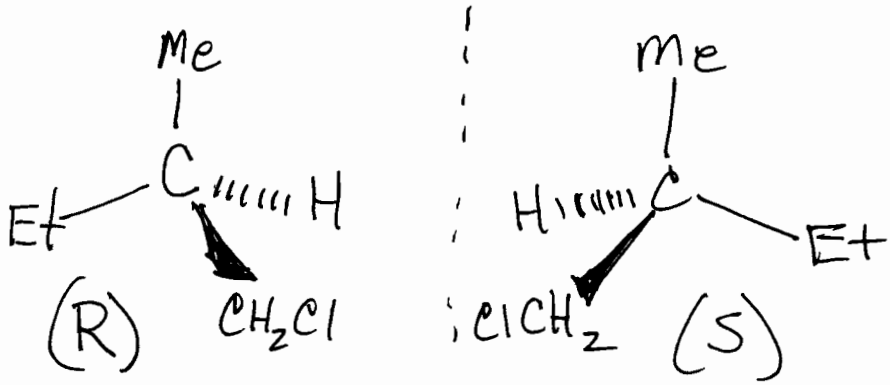
I.	(7 points)	_____
II.	(8 points)	_____
III.	(30 points)	_____
IV.	(10 points)	_____
V.	(10 points)	_____
VI.	(10 points)	_____
VII.	(8 points)	_____
VIII.	(20 points)	_____
IX.	(20 points)	_____
X.	(8 points)	_____
XI.	(10 points)	_____
XII.	(8 points)	_____
XIII.	(1 point)	_____

TOTAL (150 points) _____

I. (7 pts.) Indicate the hybridization of each carbon in these two compounds.



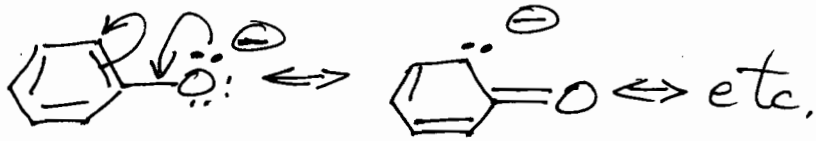
II. (8 pts.) Using wedge and dashed line 3D structures draw the two stereoisomers of 1-chloro-2-methylbutane and label each as (R) or (S).

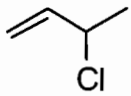
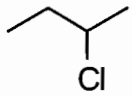


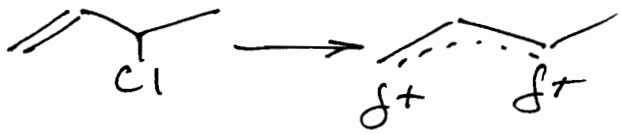
III. (30 pts.) Using structures and/or words briefly explain:

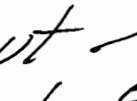
(A) Why phenol is a stronger acid than cyclohexanol (cyclohexyl alcohol)?

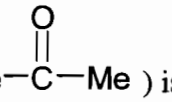
The conjugate base is resonance stabilized. i.e.



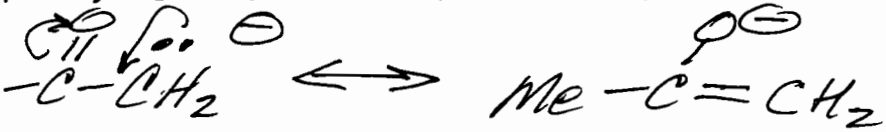
(B) Why  undergoes S_N1 reaction while  does not?



but  would only give a 2° cation.

(C) Why acetone () is more acidic than propane?

The resulting anion is stabilized by resonance delocalization.



i.e. $Me-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H_2 \longleftrightarrow Me-C=CH_2$

(D) Why $H_3CO^{\ominus}K^{\oplus}$ is a better nucleophile in an S_N2 reaction than $(CH_3)_3CO^{\ominus}K^{\oplus}$?

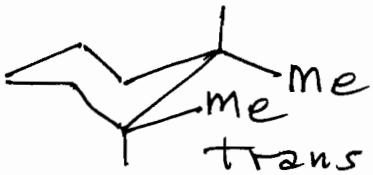
^{-}O is much more bulky which adds considerable steric strain to the T.S.

(E) Why benzene does not add bromine across any of its three double bonds?

That would destroy the aromatic character.

~~(F) Why cats sleep 17 hrs. / day?~~

(F) Why *trans*-1,2-dimethylcyclohexane is more stable than the *cis*-isomer?



trans can exist as eq-eq but cis- must be 2x -eq

(G) Why cyclohexane does not have C—C—C bond angles expected of a regular hexagon (120°)?

Because it is bent into a chair form. (i.e. not planar)

(H) Why the ΔH of hydrogenation is less for *trans*-2-butene than for the *cis*-isomer?

trans-2-butene is more stable.

(I) Why 1-butene adds HCl in a Markovnikov orientation?

That gives a more stable 2° carbocation whereas anti-Markovnikov add'n. gives 1°.

(J) Why addition of Br_2 to cyclopentene affords the *trans*-1,2-dibromo product and not the *cis*-?

Rxn. proceeds via cyclic bromonium ion intermediate.

(K) Why the substitution reactions of $R-C\equiv C^{\ominus}\ Na^{\oplus}$ are limited to methyl and primary substrates (CH_3X and RCH_2X)?

It is an SN2 rxn.

~~(L) Why a healthy dog's nose is cold?~~

(L) Why *cis*-1-bromo-3-t-butylcyclohexane will not undergo an E2 elimination of HBr?

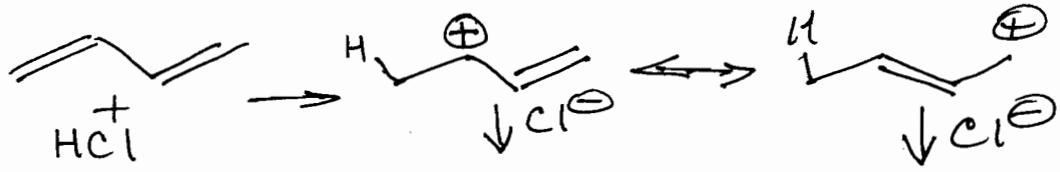
cannot ring flip to put Br in required axial position.

(M) Why the ^{1}H-NMR chemical shift of H_3C-Br is further downfield than that of CH_4?

the electronegative Br inductively removes e's which were shielding the protons.

~~(N) The answer is "stick".~~

(N) Why addition of HCl to 1,3-butadiene affords two different chlorobutenes?

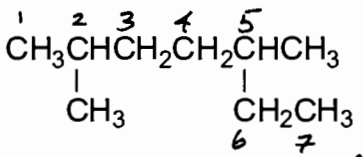


(O) Why H_2O is a liquid at 25 °C but H_2S is a gas?

H-bonding

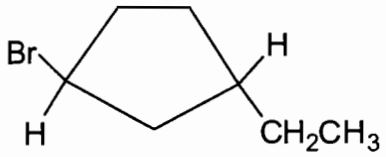
IV. (10 pts.) Provide proper names for the following compounds.

(A)



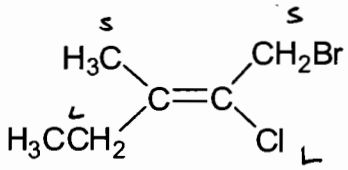
2,5-dimethylheptane

(B)



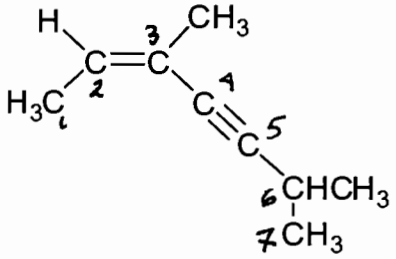
trans-1-bromo-3-ethylcyclopentane

(C)



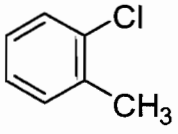
(Z)-1-bromo-2-chloro-3-methyl-2-pentene

(D)



(Z)-3,6-dimethyl-2-pentene-4-yne

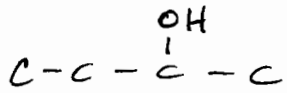
(E)

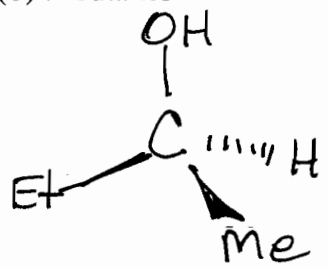


o-chlorotoluene

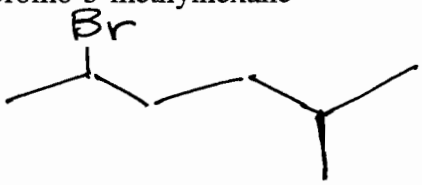
V. (10 pts.) Provide the structures that correspond to the following names.

(A) (S)-2-butanol

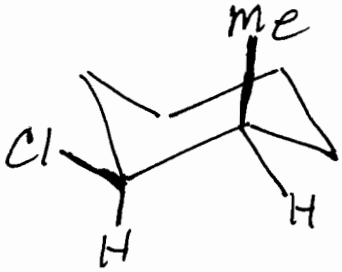




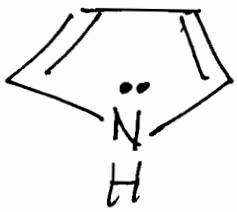
(B) 2-bromo-5-methylhexane



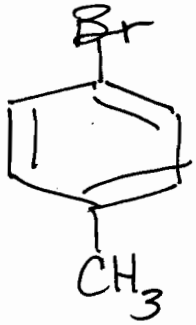
(C) *cis*-1-chloro-2-methylcyclobexane (use chair form)



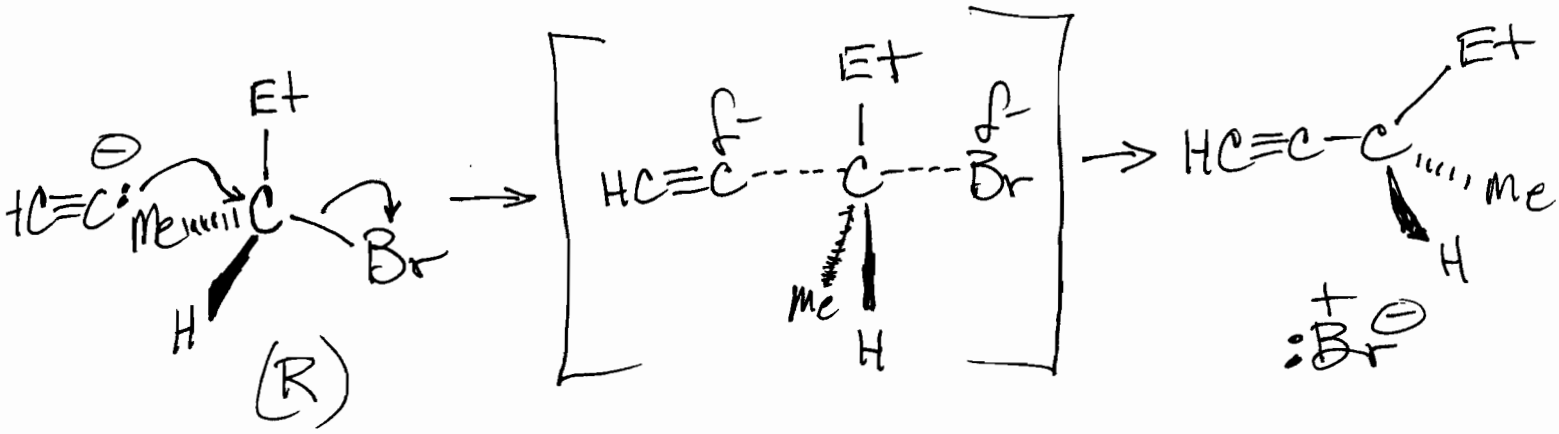
(D) pyrrole



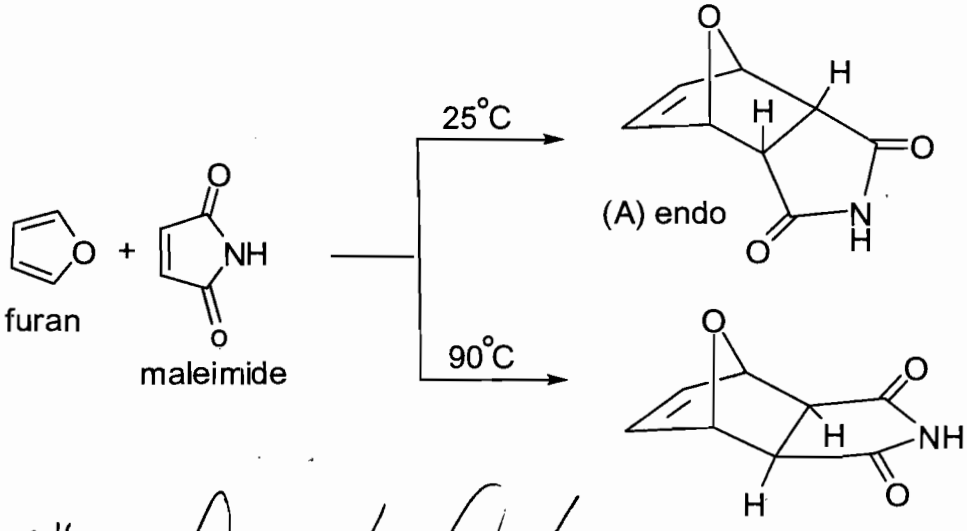
(E) p-bromotoluene



VI. (10 pts.) Using wedge and dotted line structures and arrows for electron pair movement provide a detailed mechanism of the S_N2 reaction of $HC{\equiv}C{:}^{-}\ Na^{+}$ and (R)-2-bromobutane. Include structure(s) of any transition state(s) in your mechanism.



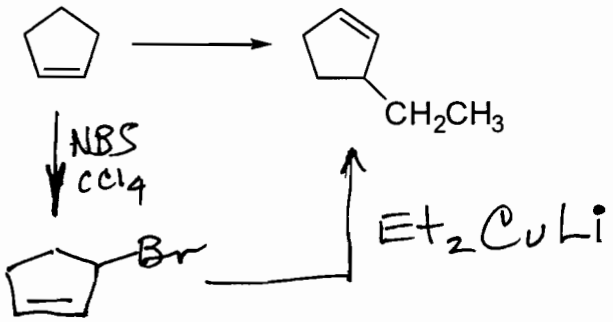
VII. (8 pts.) When furan and maleimide undergo a Diels-Alder reaction at 25 °C the major product is endo-adduct A, but when the reaction is conducted at 90 °C the major product is exo-adduct B. Explain what is happening here in no more than two sentences.



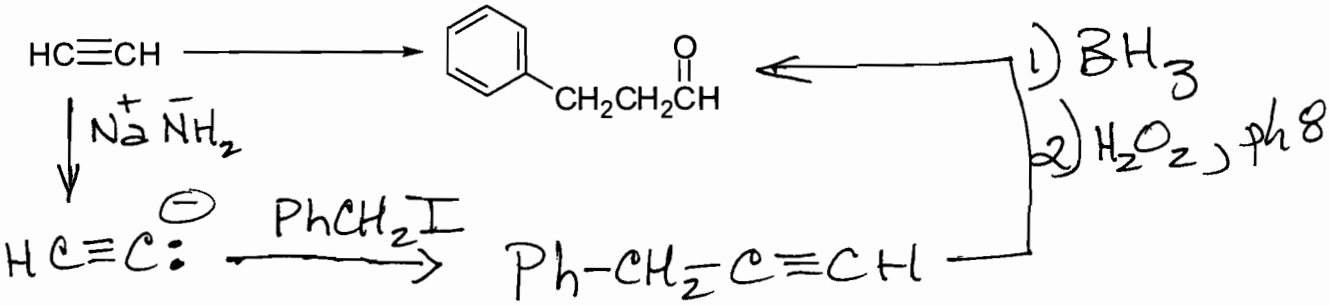
"A" is formed faster and is the "kinetic product", while at 90°C the system is in equilibrium and the more stable or "thermodynamic product", "B" predominates.

VIII. (20 pts.) Show how you would carry out the following synthetic transformations assuming the availability of all necessary reagents.

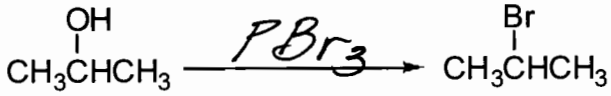
(A)

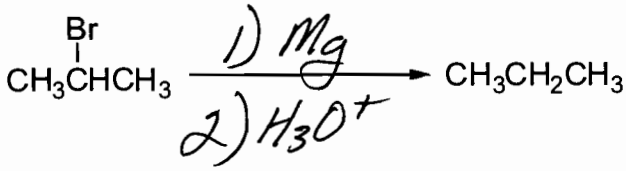


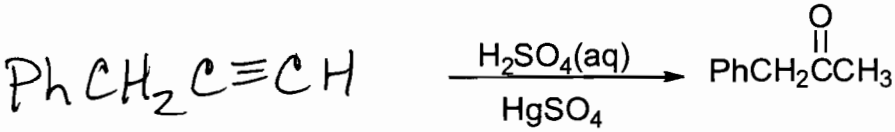
(B)

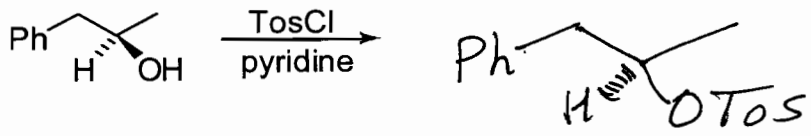


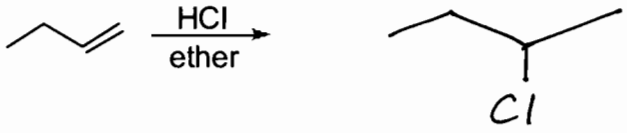
IX. (20 pts.) Complete the following reactions.

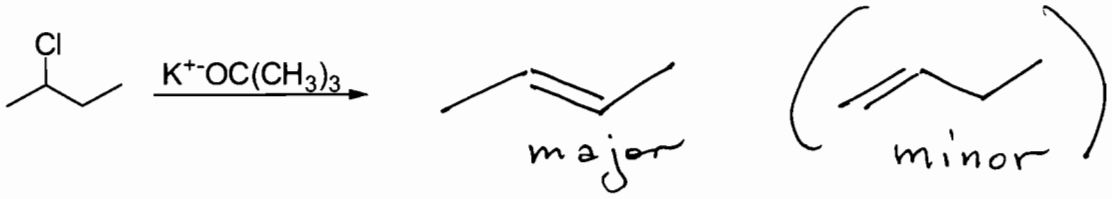
(A) 

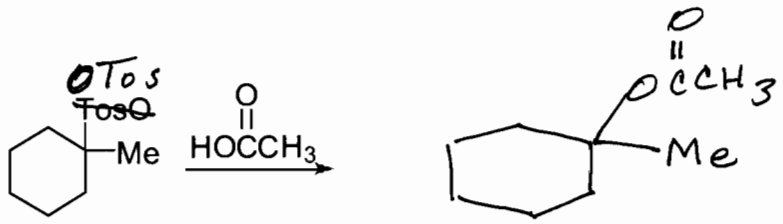
(B) 

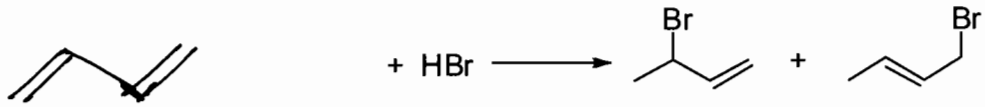
(C) 

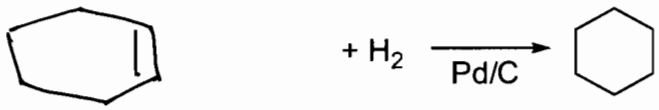
(D) 

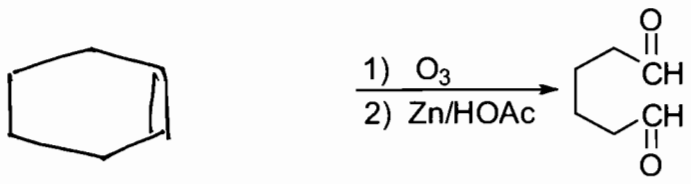
(E) 
HCl
ether
Cl

(F) 
Cl
K+-OC(CH3)3
major
minor

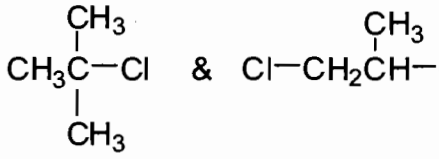
(G) 
OTos
TosO
Me
O
HOCCH3
O
OCCH3
Me

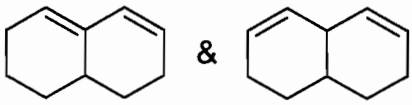
(H) 
+ HBr
Br
+
Br

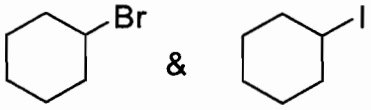
(I) 
+ H2
Pd/C

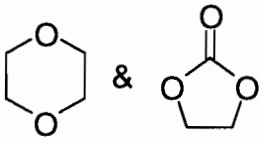
(J) 
1) O3
2) Zn/HOAc
O
CH
CH
O

X. (8 pts.) Indicate which spectral technique, NMR, IR, UV or MS, would most readily allow differentiation between the compounds in each pair of compounds below.

(A)  NMR

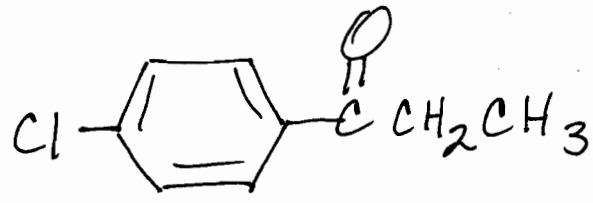
(B)  UV

(C)  MS

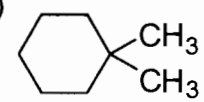
(D)  IR

C_9H_9OCl

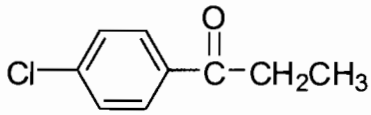
XI. (10 pts.) A compound of unknown structure is found from its mass spectrum to have a molecular formula of C_8H_7OCl. Its IR shows a strong absorption at 1691 cm^{-1} and the ^{1}H-NMR consists of a triplet at 1 δ (3H), a quartet at 2.6 δ (2H) and two doublets (each 2H's) centered at 7.6 δ. What is the structure?



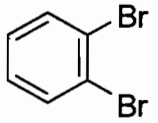
XII. (8 pts.) How many ^{13}C resonance peaks would you observe in the broadband-decoupled spectra of each of the following compounds?

(A) 

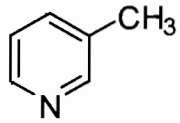
5

(B) 

7

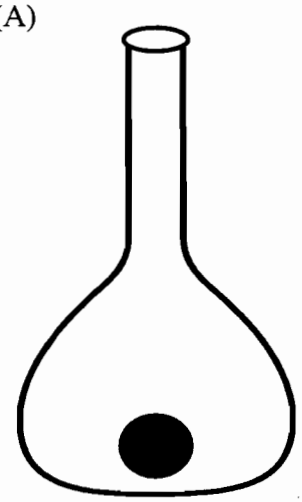
(C) 

3

(D) 

6

XIII. (1 pt.) Guess how many marbles there are in the jar.

(A) 

1 (±1)

(B) What do you call a boomerang that doesn't work? (~~See 3N~~)

stick