Dr. Steven Pedersen October 2, 2002

Chemistry 3A

Midterm #1

Student name: Key

Student signature: _____

TA's name or section number: _____

Problem 1 _____ (30 pts)

Problem 2 _____ (30 pts)

Problem 3 _____ (30pts)

Problem 4 _____ (30 pts)

Problem 5 _____ (40 pts)

Problem 6 _____ (40 pts)

Total Points _____ (200 pts)

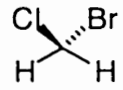
No Calculators Allowed
Be Sure Your Exam has 12 Pages
Be Sure To Try All Parts of Each Problem!

Bond Dissociation Energies of Various Bonds

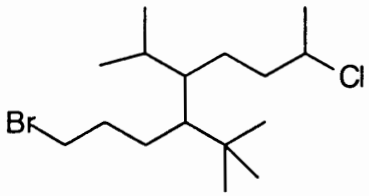
Bond	DH° (kcal/mole)	Bond	DH° (kcal/mole)
Primary C-H	101	Tertiary C-Br	70
Secondary C-H	98.5	Br_2	46
Tertiary C-H	96.5	HBr	87
Primary C-Br	70		
Secondary C-Br	70		

Organic Lingo

1A. Provide a systematic name for the following compounds. Use common nomenclature for any branched substituents. (30 pts)



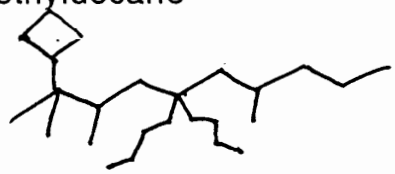
Bromochloromethane (3)



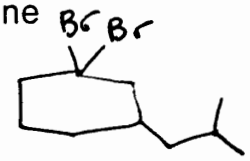
9-bromo-6-tert-butyl-2-chloro-5-isopropyl-nonane (3)

B. Draw a structure for the following names. For cycloalkanes use flat rings. For all others use bond-line notation.

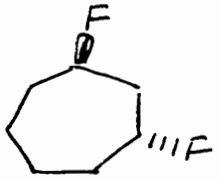
- 2-cyclobutyl-5,5-dibutyl -2,3,7-trimethyldecane

 (3)

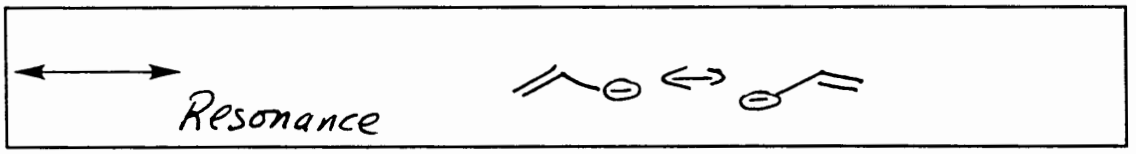
- 1,1-dibromo-3-isobutylcyclohexane

 (3)

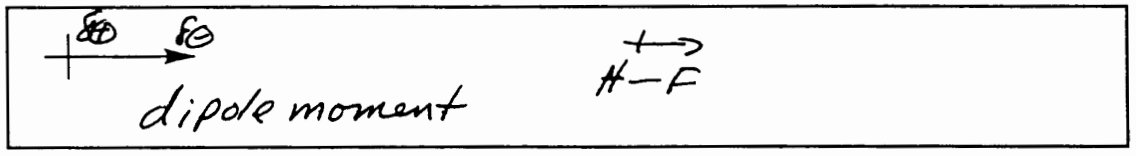
- trans-1,3-difluorocycloheptane

 (3)

C. We have used many types of arrows to describe various phenomena. In the boxes below, identify each arrow using only a FEW words AND provide a REAL example of how it could be used.



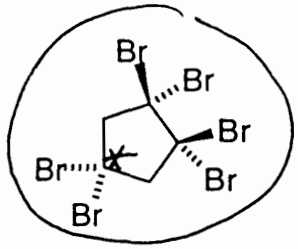
(4)



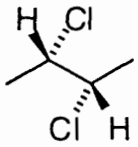
(4)

D. One or more of the bond-line structures shown below contain improper use of wedge-dash notation. Circle the incorrect one(s) AND explain why they are incorrect.

(4)



This says that both bromines on the labeled carbon are going behind the paper



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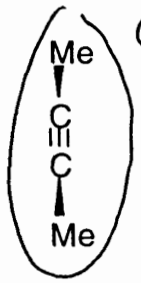


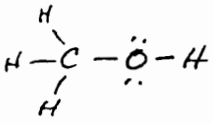
The entire molecule would be linear, not bent like the wedges suggest.

The Name is Bond. Molecular Bond.

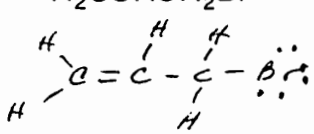
2. (0 pts)

A. Write the Lewis dot structures for each of the following molecules. Be sure to SHOW ALL BONDING AND NON-BONDING ELECTRONS AND CHARGES.

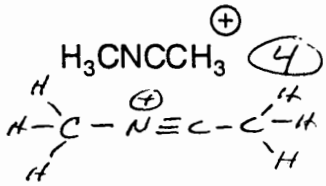
MeOH (4)



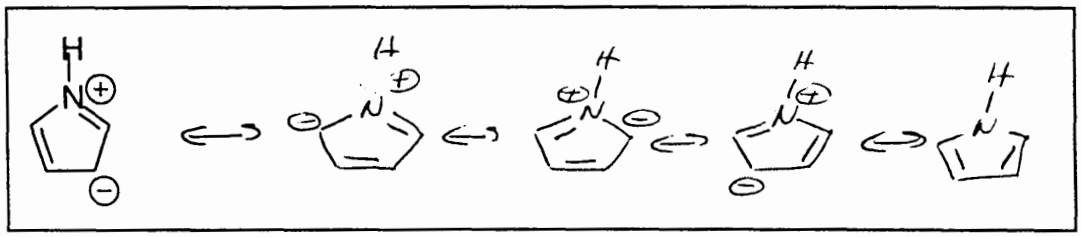
H_2CCHCH_2Br (4)



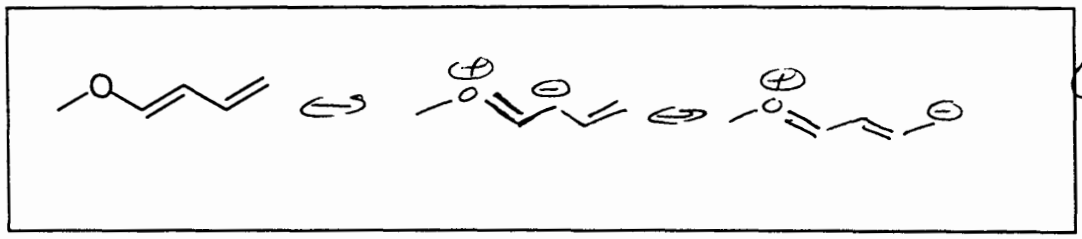
H_3CNCCH_3 (4)



B. Draw two additional resonance structures for each of the following molecules. Your structures must be reasonable.



(9)



(9)

AO/MO

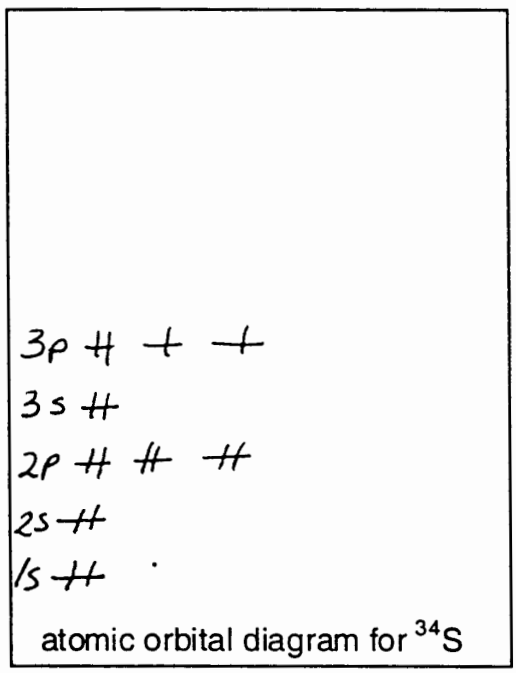
3. (30 pts)

A. Which term best describes the $2P_x$, $2P_y$ and $2P_z$ atomic orbitals (circle one):

valence nodeless Hund's rule

(3) regenerate **degenerate** primordial

B. Draw the atomic orbital energy level diagram for 1S through 3P. On the diagram fill in the electrons for ^{34}S (atomic number 16). How many neutrons does ^{34}S have?



number of neutrons in ^{34}S 18

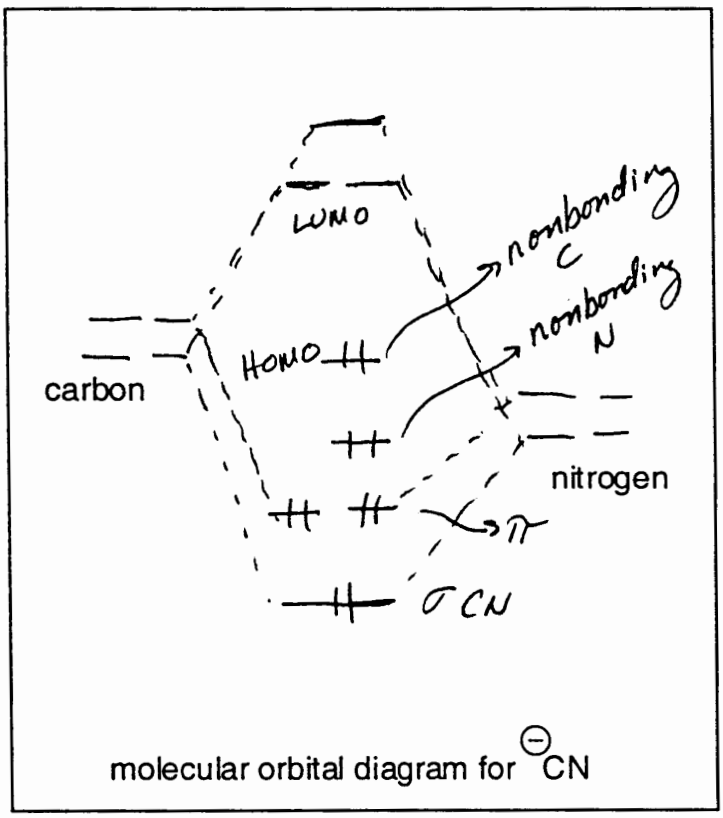
(3)

3 for correct levels

3 for correct # of electrons

C. Construct the molecular orbital diagram for the cyanide ion, ^{-}CN, using the following guidelines and labeling schemes. BE SURE TO INCLUDE EVERYTHING ASKED FOR BELOW.

- Assume that both the carbon and nitrogen are SP hybridized.
- The relative energies for carbon and nitrogen are provided below.
- Indicate the relative energy levels of any atomic and hybrid orbitals on the left and right hand sides of the diagram.
- Clearly indicate which orbitals are being combined to make molecular orbitals.
- Fill in all of the electrons.
- Label all the levels as σ, π, etc.
- Label the HOMO and LUMO



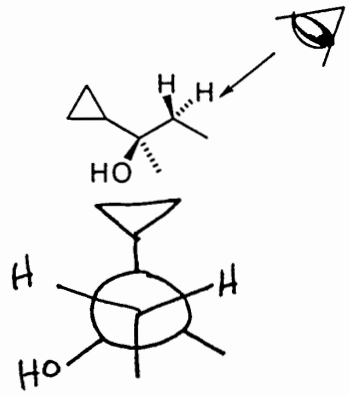
molecular orbital diagram for $^{\ominus}CN$

18 pts

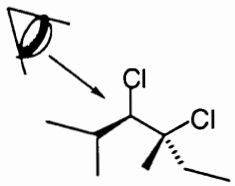
Freely Rotating

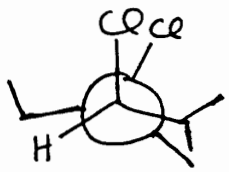
4. (30 pts)

A. Draw Newman projections for the bond line structures shown below. Make sure your projection is representative of the conformation shown.



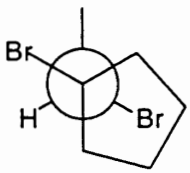
(5)

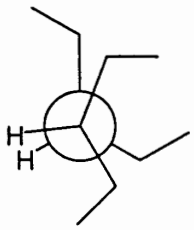




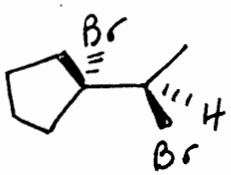
(4)

B. Draw bond-line structures, including wedges and dashes, that exactly represent the conformations depicted by the following Newman projections.



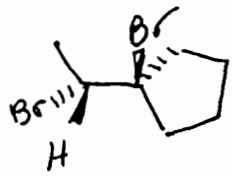


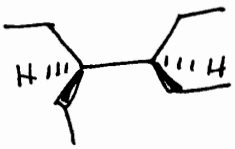
eclipsed



(5)

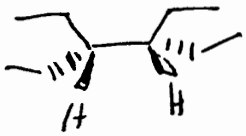
OR



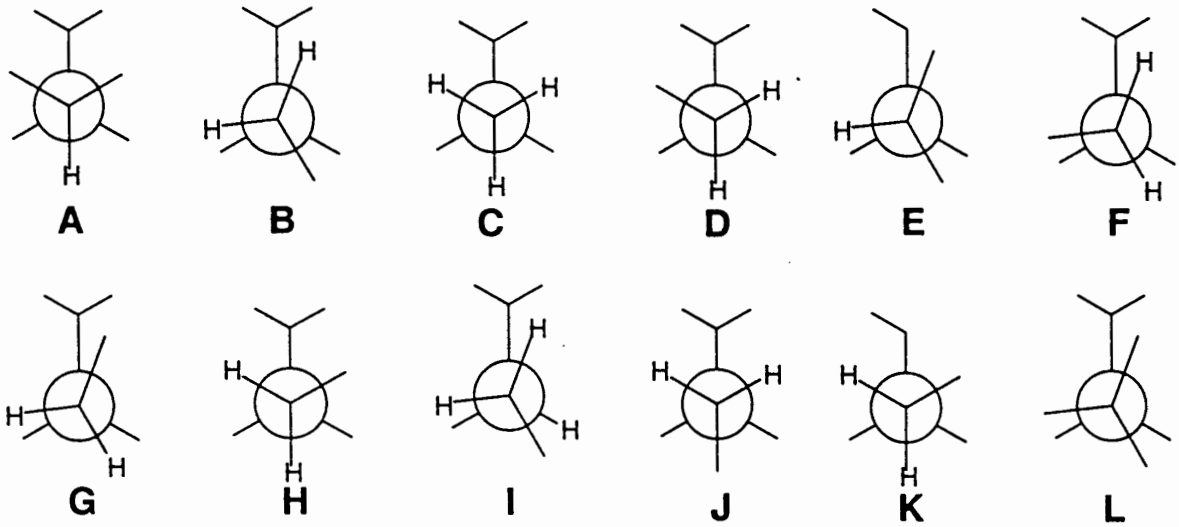


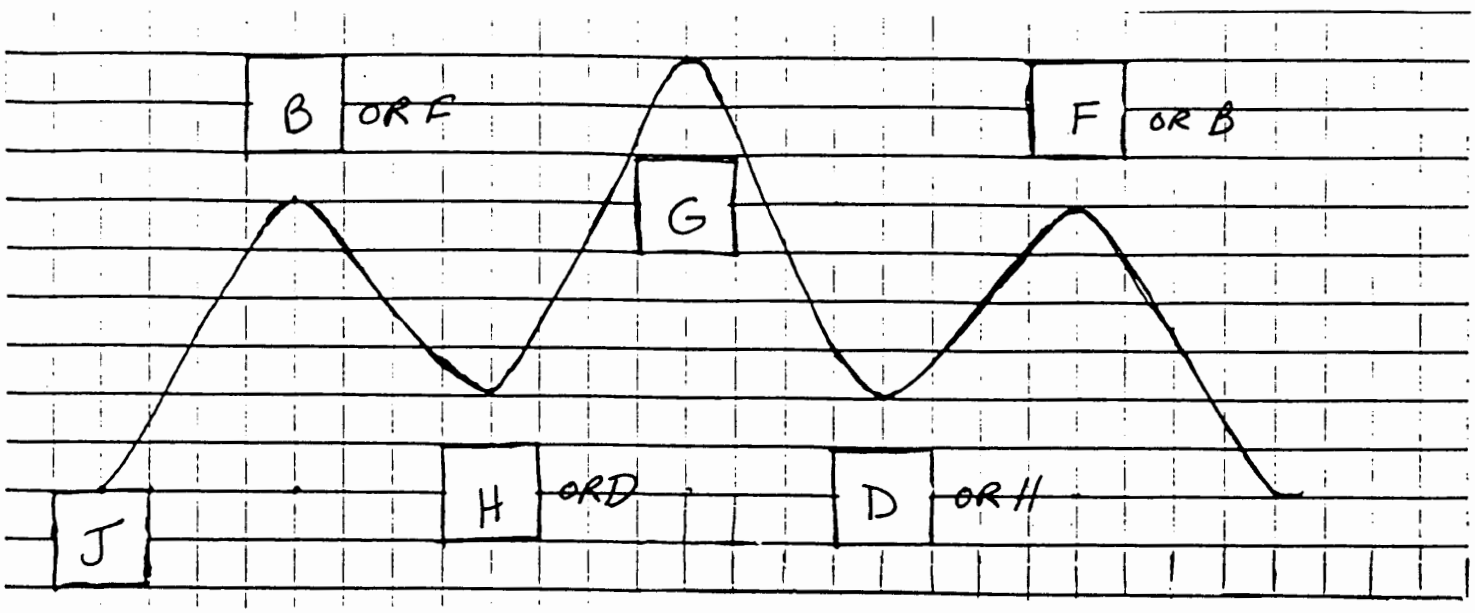
OR

(4)



C. Below is a potential energy diagram that reflects the relative energies associated with rotation about the C_4-C_3 bond of 2,3,3-trimethylpentane. Match the Newman projection with each minimum and maximum on the diagram (put the letters in the boxes). Be sure to rotate in only one direction. **Hint:** Start by eliminating Newman projections that do not match the molecule in question.

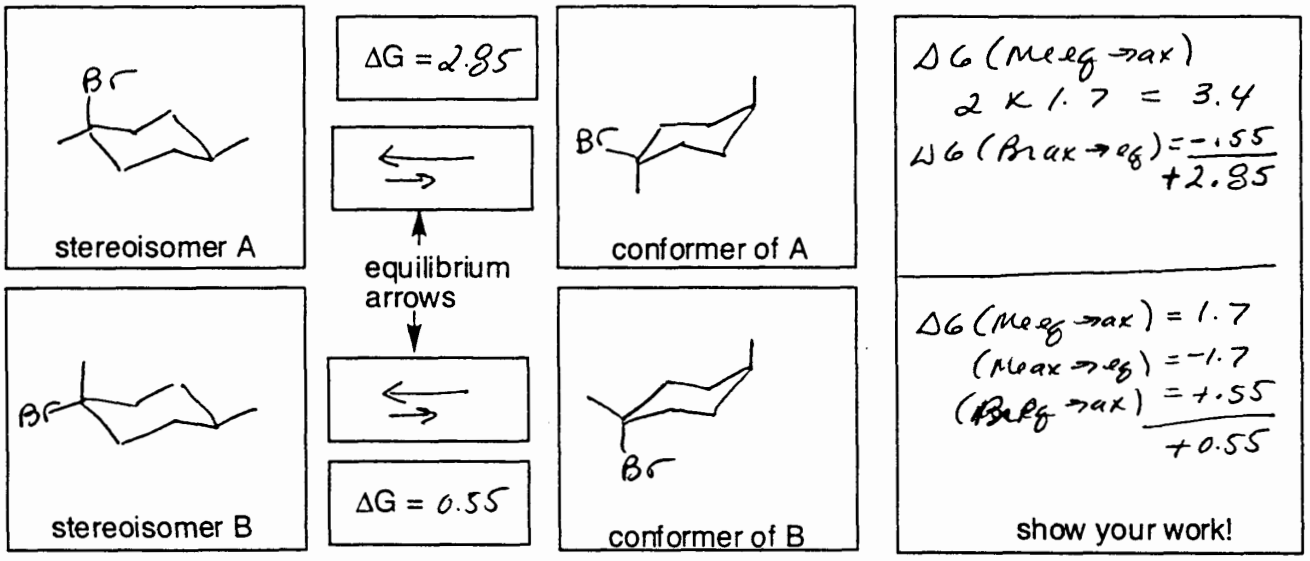




2 each for 12 total

E. In the boxes labeled stereoisomer A and B, draw the CHAIR structures for the two stereoisomers of 1-bromo-1,4-dimethylcyclohexane, the product in part A.

2pts for each box



F. In the boxes labeled conformer A and B, draw the ring-flipped conformations of stereoisomers A and B.

G. Calculate ΔG for each conformational equilibrium. Place your answer in the boxes labeled ΔG =. In order to receive any credit you must show your work.

H. Using appropriate arrows indicate which side the equilibrium would lie on for each case.

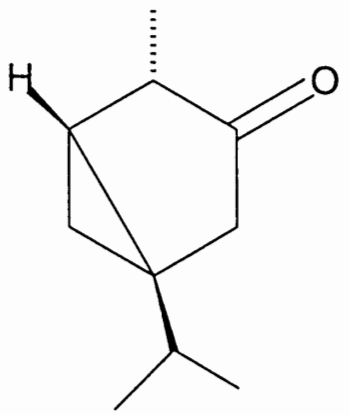
TABLE 4-3 Change in Free Energy on Flipping from the Cyclohexane Conformer with the Indicated Substituent Equatorial to the Conformer with the Substituent Axial

Substituent	$\Delta G°$ (kcal mol^{-1})	Substituent	$\Delta G°$ (kcal mol^{-1})
H	0	F	0.25
CH_3	1.70	Cl	0.52
CH_3CH_2	1.75	Br	0.55
$(CH_3)_2CH$	2.20	I	0.46
$(CH_3)_3C$	≈ 5	HO	0.94
HO—C(=O)	1.41	CH_3O	0.75
CH_3O—C(=O)	1.29	H_2N	1.4

Note: In all examples, the more stable conformer is the one in which the substituent is equatorial.

Absinthe

6. Most countries banned the green liquor known as absinthe at the turn of the century due to the presence of thujone, a hallucinogen that, if abused, can lead to serious medical complications. All of the following questions are related to this molecule. (40 pts)



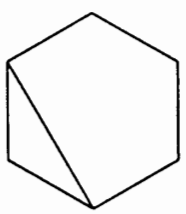
thujone

A. Would you describe the relationship between the methyl and isopropyl groups in thujone as (circle one):

cis (trans) resonance equilibria (2)

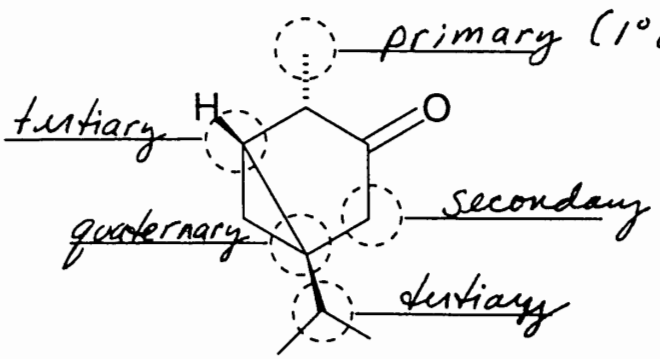
conformers rotamers

B. Provide a systematic name for the core of thujone.



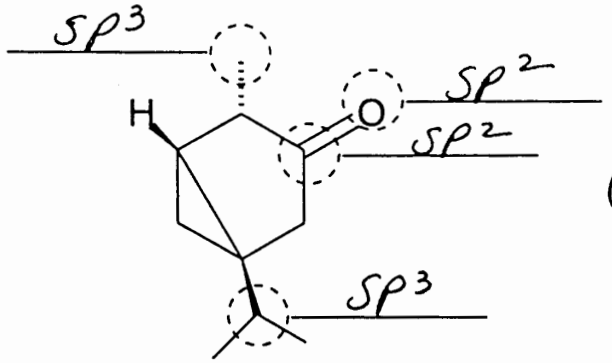
NAME: bicyclo[3.1.0]hexane (3)

C. On the structure below label each of the circled carbons as primary, secondary, tertiary or quaternary.



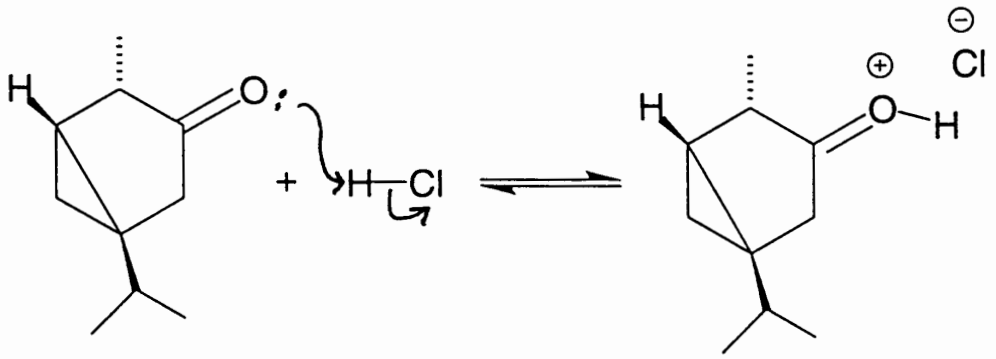
1 each

D. On the structure below describe the hybridization at each circled atom.



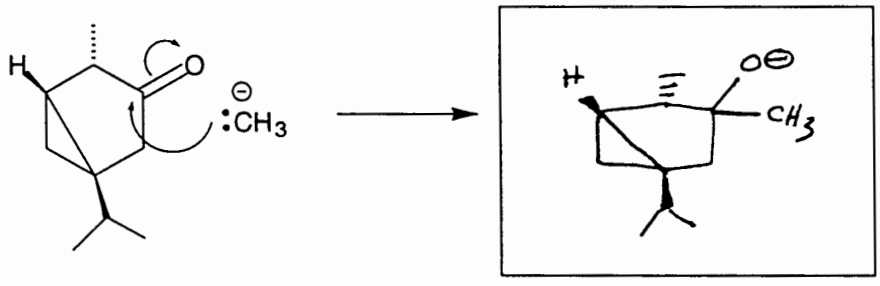
1 each

E. Draw an arrow-pushing mechanism that is consistent with the following reaction.



4

F. Show the product you would expect to get from the following arrow-pushing mechanism.



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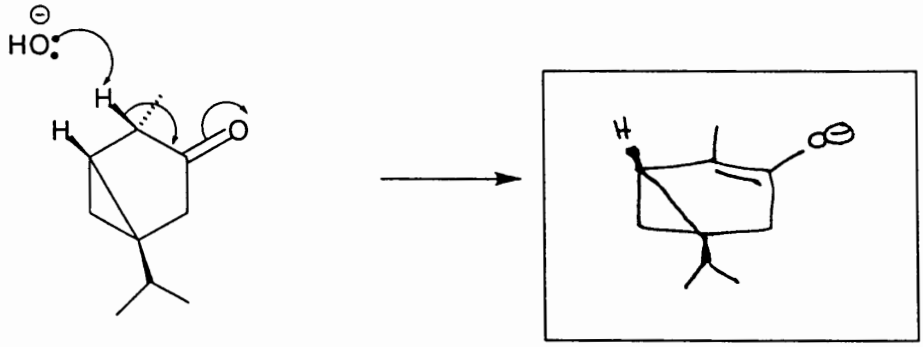

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