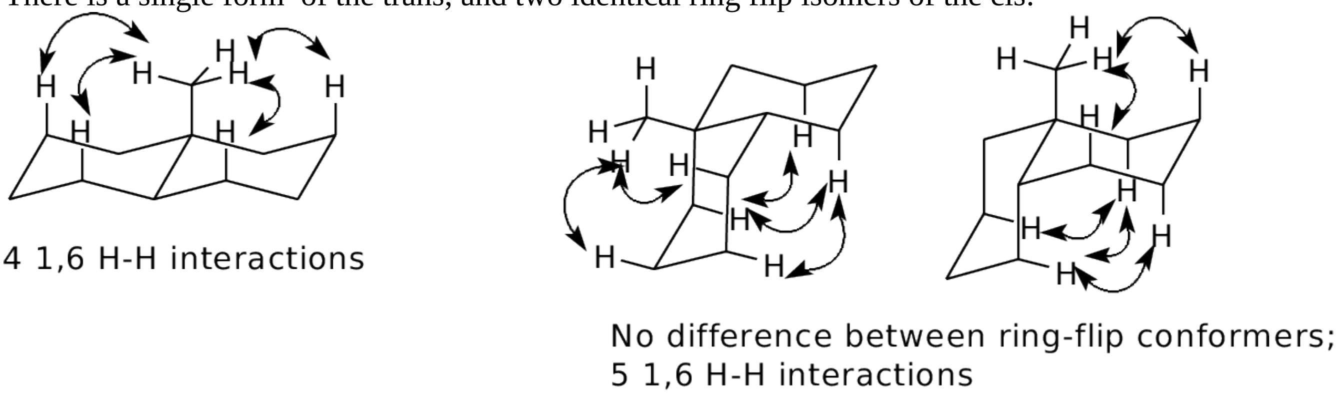
CH 630
Midterm Exam 1
Answer Key

Please write answers in the blue books provided; you may keep the exam paper unless there is anything written on it you wish graded.

You may use numerical calculators, molecular models and/or drawing templates, but no notes, books or other materials containing chemical information.

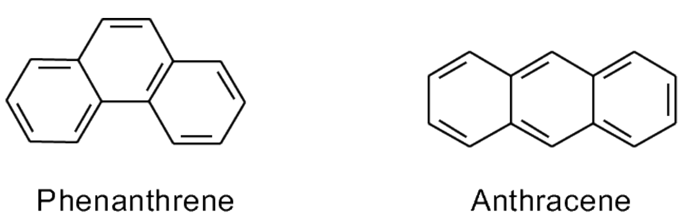
1. (20 points) Quantitatively estimate the enthalpy difference between cis and trans-1-methyldecalin (1-methylbicyclo-[4.4.0]-decane). (Hint: begin by drawing 3-D structures of all conformers for each.)

There is a single form of the trans, and two identical ring flip isomers of the cis:

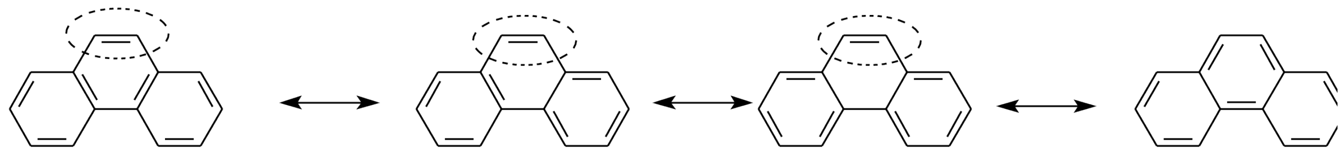


Count the 1,6 H-H interactions (there are no 1,7 H-H interactions) and subtract; the cis is uphill by 0.9 kcal/mol.

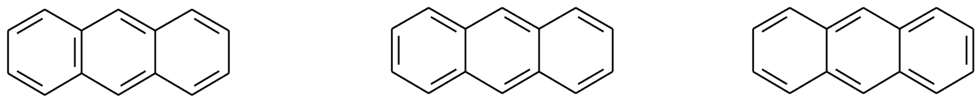
2. (20 points) Use your understanding of bonding to explain why phenanthrene behaves more like an alkene when compared to its isomer anthracene.



Compare aromaticity in forms that delocalize the central bond. Anthracene maintains the same degree of aromaticity regardless of resonance:



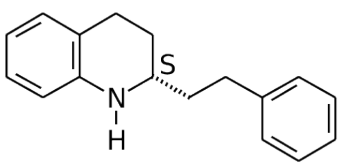
3 rings aromatic | 2 rings aromatic | 2 rings aromatic | 1 ring aroma



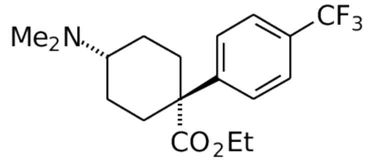
No "isolated" double bond: perimeter is aromatic in 2 of 3 forms

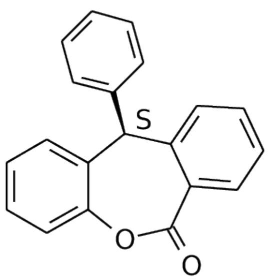
3. (24 points) Assign all stereogenic centers (R or S) in each molecule, and indicate whether the molecule is chiral or achiral.

Chiral

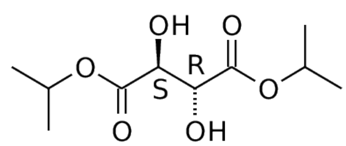


Achiral



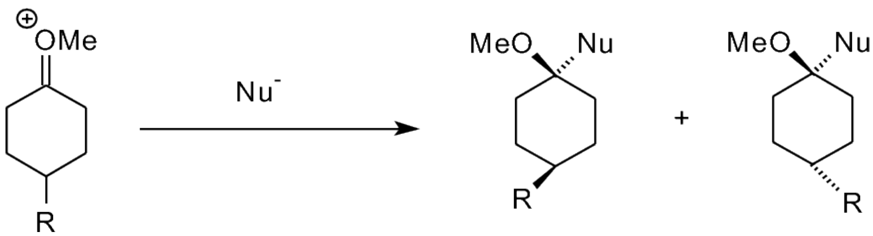


Chiral



Achiral (meso)

4. (36 points) Consider the reaction of nucleophiles with the following stabilized carbocation (generated under SN1 conditions):



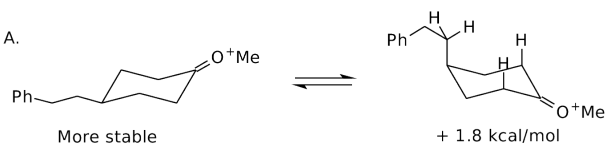
A. Draw the two dominant conformers of the carbocation, and indicate which is the more stable for $R{=}CH_2CH_2Ph$.

B. Draw the two dominant conformers of the carbocation, and indicate which is the more stable for $R{=}OCH_2Ph$.

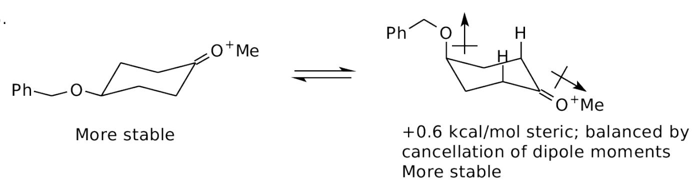
C. Draw the conformations of the possible products for $R{=}CH_2CH_2Ph$ and $Nu = CH_2{=}CH{-}CH_2^-$.

D. Draw the conformations of the possible products for $R{=}OCH_2Ph$ and $Nu = CH_2{=}CH{-}CH_2^-$.

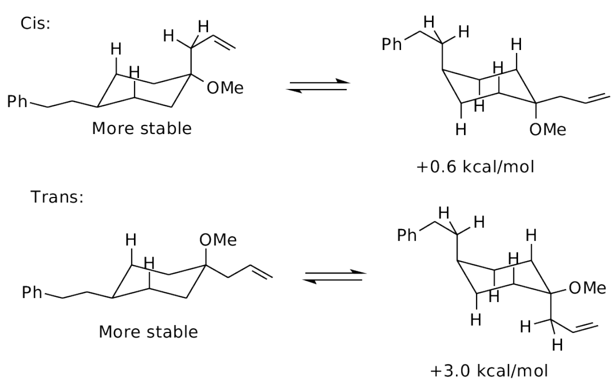
A.



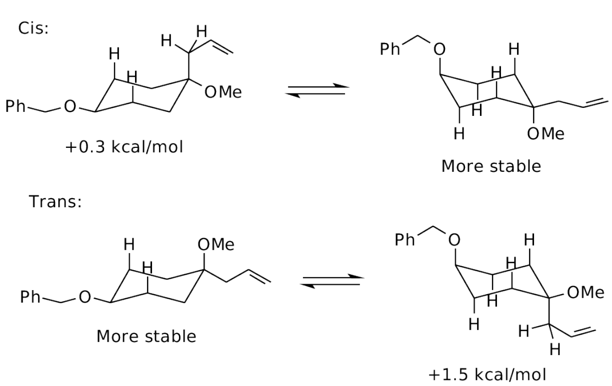
B.



C.

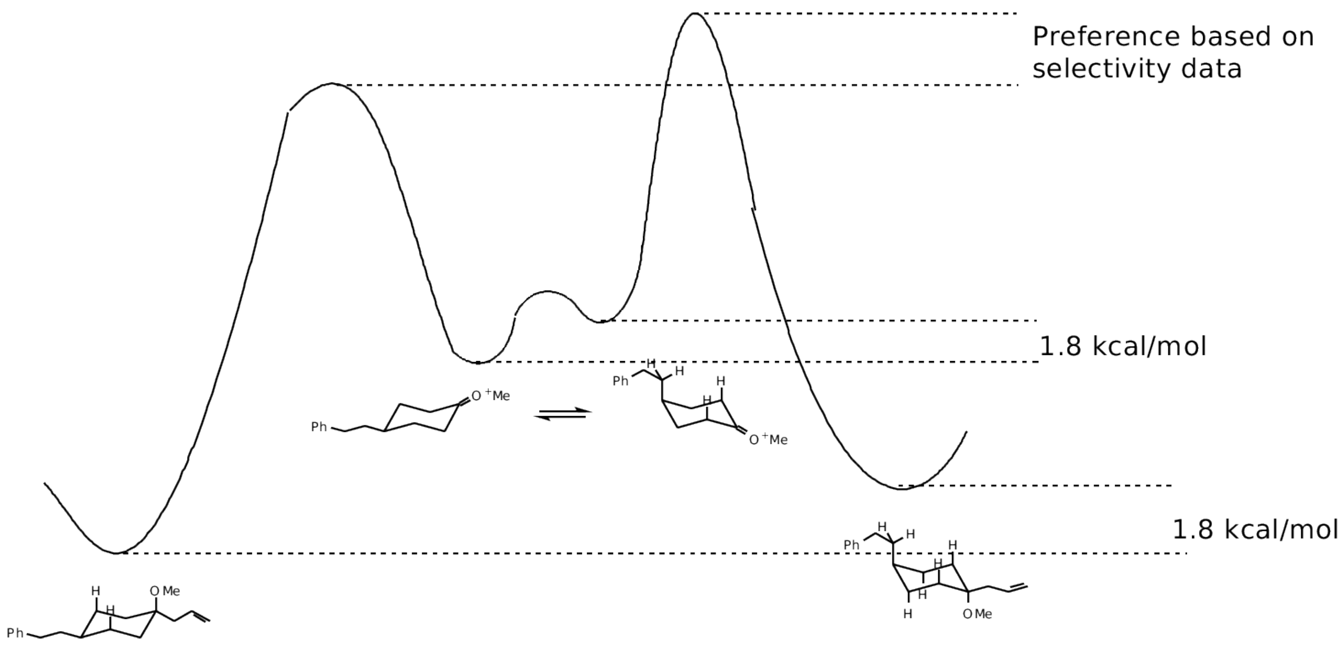


D.

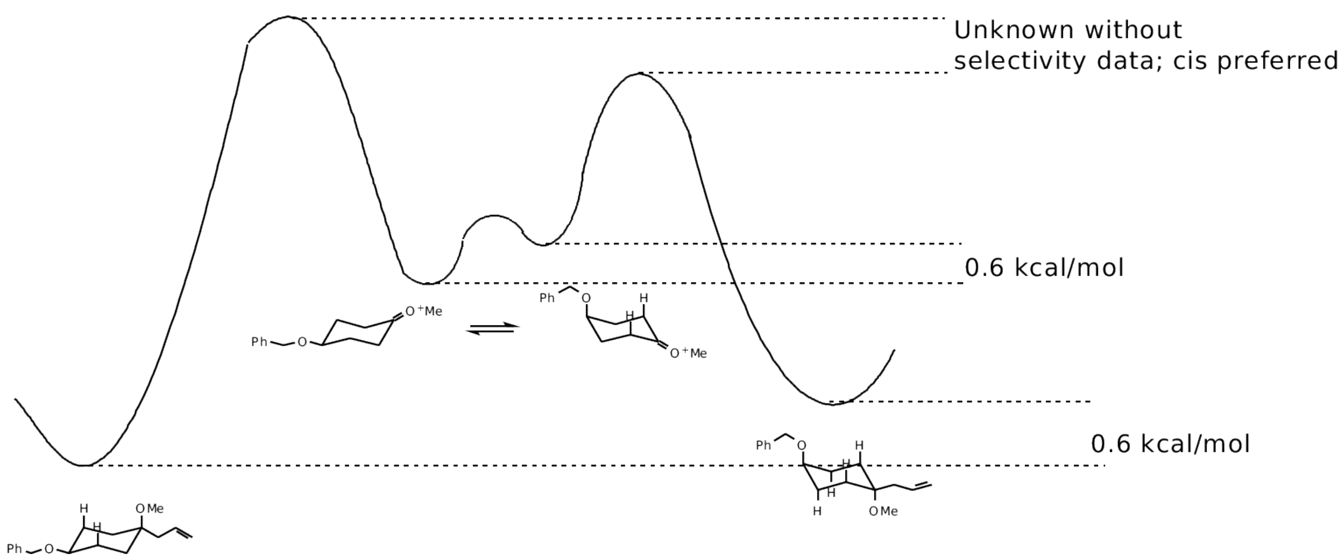


E. Choose one of either case in (C, D), and draw potential energy diagrams for the possible reaction outcomes.
Here are the two PE diagrams:

From C:



From D:



F. The experimental outcome is shown below. Explain whether the Curtin Hammett principle applies to the case you chose to illustrate. If more information is needed, specify what additional thing(s) you would need to know in order to reach a conclusion.

R	Cis	Trans
CH_2CH_2Ph	5%	95%
OCH_2Ph	80%	20%

For the phenethyl case (C), the thermodynamic product is preferred. One would need to know the equilibrium ratio (in the first place) and resubject one of the products to reaction conditions to know whether thermodynamic control were in effect.
However, the benzyloxy case (D) provides the less-thermodynamically preferred product and therefore must be under kinetic control. One could infer from this that C is under kinetic control as well.