

1. In an  $S_N2$  reaction, what is meant by *inversion of configuration*? (5 points)

2. What is the *order* of the a reaction with the following rate law expression? (5 points)

$$\text{Rate} = k[A]^2[B]$$

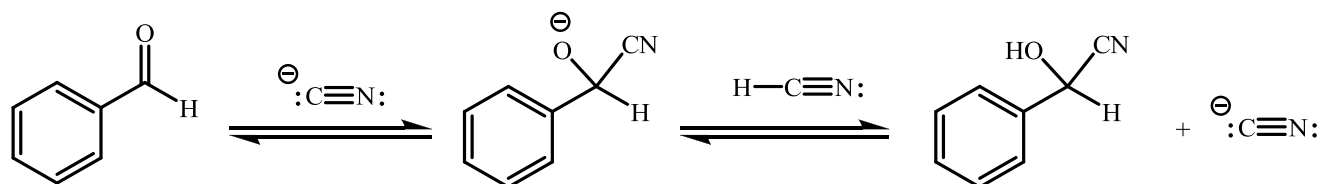
3. Given the rate law above in question 2, what can you say about the transition state with regard to reactants A and B if the stoichiometry is as shown below? (5 points)



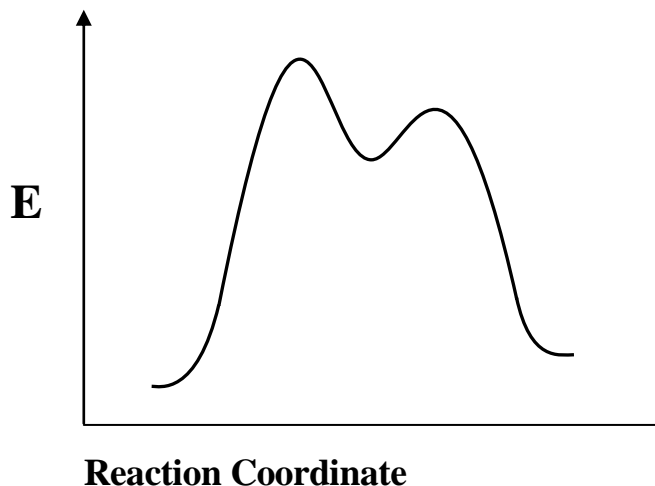
4. With regard to substitution reactions, what is meant by the term *ion-pairing*? (5 points)

5. Why are *tertiary* carbocations more stable than *secondary* carbocations? Explain (use more than one word!) (5 points)

6. For the following reaction, label each step as either a *proton transfer*, *nucleophilic attack*, *loss of leaving group*, or *carbocation rearrangement* and show the electron pushing for each step. (10 points)



7. Consider the following reaction and its energy diagram. (24 points)



Show the following on the energy-level diagram above:

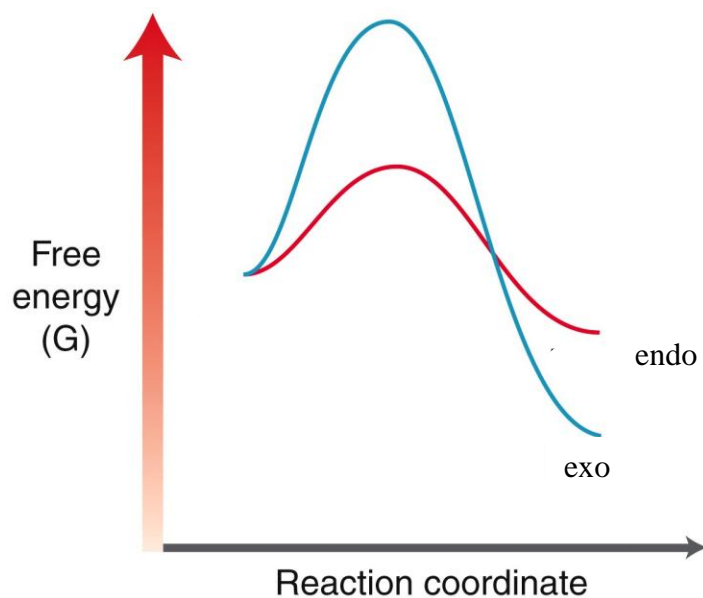
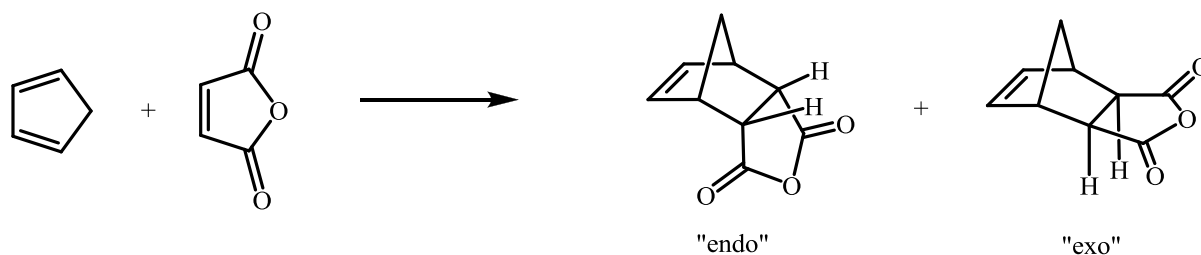
- The activation energy for each step ( $E_{a1}$  and  $E_{a2}$ )
- The Gibbs free energy for each step ( $\Delta G_1$  and  $\Delta G_2$ )
- The overall free energy ( $\Delta G_{\text{overall}}$ ).
- Where the transition states for each step ( $TS_1$  and  $TS_2$ ) are.
- Where the reagents (A), intermediates (B, C), and products (D) would appear on the graph.

Answer the following questions about the reaction depicted in the diagram:

- Is the overall reaction spontaneous in the forward direction? *Explain.*
- Which step is rate-limiting? *Explain.*
- For the overall reaction, is  $K_{\text{eq}} > 1$  or  $< 1$ ? *Explain.*

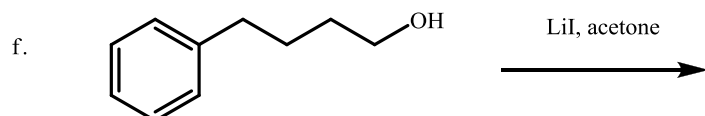
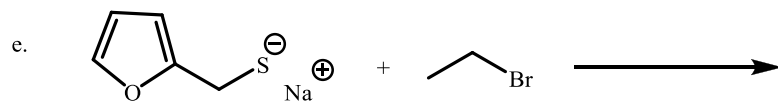
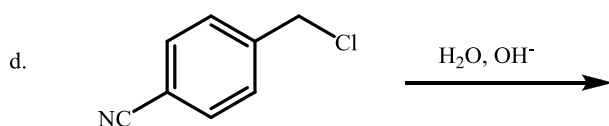
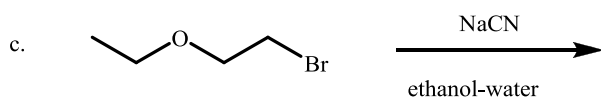
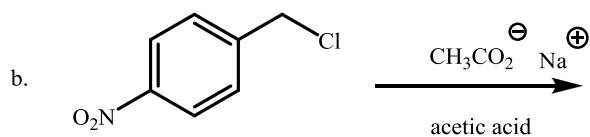
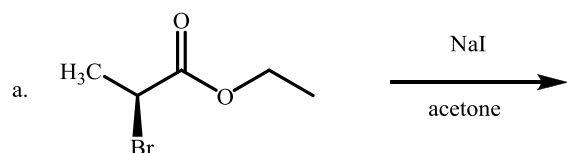
8. For the following reaction (known as the Diels-Alder reaction), there are two possible products labelled as *endo* and *exo*. The energy diagram is shown. (Hint:  $\Delta G = \Delta H - T\Delta S$ )
- Does this reaction show kinetic vs. thermodynamic control? Explain
  - Which product should be favored if the reaction is run at low temperatures?
  - Which product should be favored at higher temperatures?

(15 points)



(Source: From Klein, *Organic Chemistry*, 1<sup>st</sup> Edition, Wiley, 2011, p. 250)

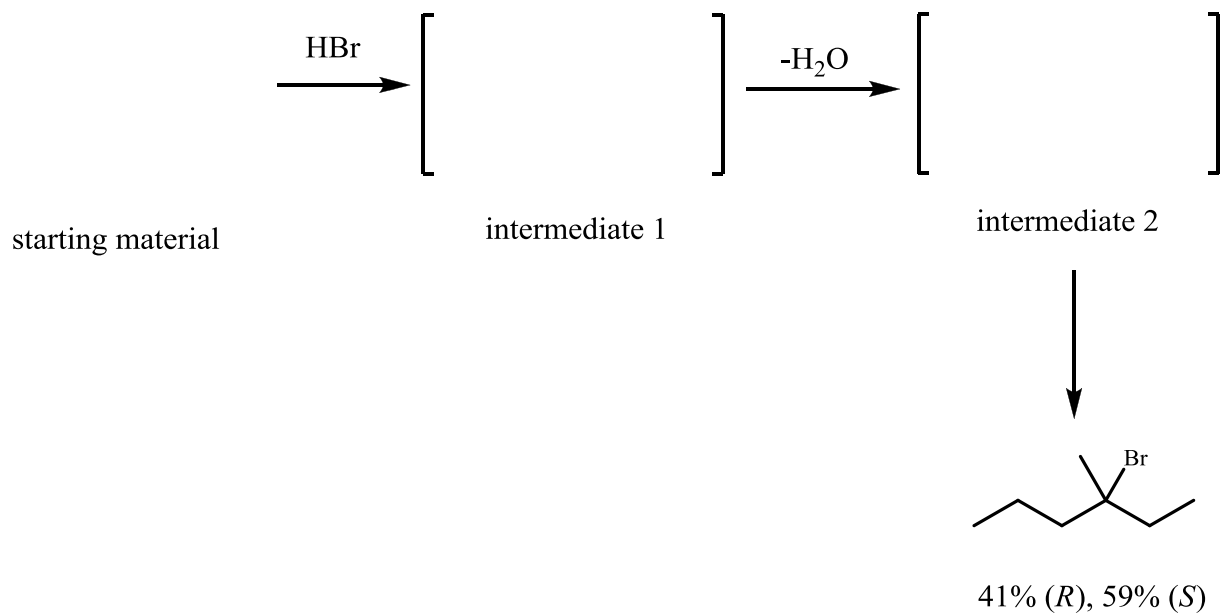
9. Draw the expected product(s) from the following reactions. Show stereochemistry where necessary. If no reaction is expected, write NR. (30 points)



10. Draw the transition state for the following *exothermic*  $S_N2$  reaction. Be extremely clear and as detailed about the geometry as possible. (Hint: use the Hammond postulate) (10 points)

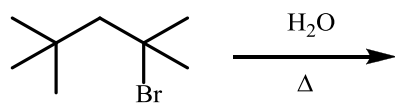


11. Show the structures of the starting material and both intermediates from the following substitution reaction. (note the stereochemistry indicated for the product) (15 points)



12. The order of nucleophilic strength for the halides is  $F^- > Cl^- > Br^- > I^-$  in *polar aprotic* solvents like DMSO, but is reversed in *polar protic* solvents like methanol ( $CH_3OH$ ). Explain why. (10 points)

13. Does the  $S_N1$  reactions shown below involve a carbocation rearrangement? Show the product(s) (10 points)



14. In terms of the mechanism, explain why the two products are formed. (10 points)

