Statistics: High score, average and low score will be posted on the course web site after exam grading is complete.

A note about exam keys: The answers presented here may be significantly longer than expected from a student taking the exam. An exam key serves not only to reveal what was expected, but to instruct you as well.

To see the projected course grade cutoffs, consult the grading scale on the Chem 14D course web page.

1. (a) Catalytic hydrogenation. Results in syn addition of H₂.
   (b) Acid-catalyzed alkene hydration. Results in Markovnikov addition of water.
   (c) Ozonolysis. Cleaves carbon-carbon double bond, producing two carboxyls.
   (d) Friedel-Crafts acylation. Tert-butyl is a large ortho/para director.
   (e) EAS chlorination. Despite being a strong deactivator, fluorine is still an ortho/para director.
   (f) Free radical halogen. Occurs mostly at the site involving the most stable radical intermediate.
   (g) Anti-Markovnikov addition of HBr via a radical mechanism.

2. Bromine radical \( \cdot \text{Br} \) or \( \cdot \text{Br} \).

3. Ph-\( \equiv \text{C} \text{C}=\equiv \text{C} \text{CH}_3 \) → Ph-\( \equiv \text{C} \text{C}=\equiv \text{C} \) → Ph-\( \equiv \text{C} \text{C}=\equiv \text{C} \) (also anti addition)
4. Among reactions A, B, and C, reaction B makes the most sense. The mechanism of reaction A involves an unlikely carbocation rearrangement (3° to 2°). Reaction C is utterly impossible because the starting alkene has eight carbon atoms whereas the product has only seven carbon atoms.

5. Among reactions D, E, and F, reaction E is the fastest reaction. Reaction E’s rate-determining step (alkene protonation) leads to the most stable carbocation (3° with resonance).

6. The OCH₃ group is an ortho/para director. The OCH₃ and NO₂ groups are both fairly small so the ortho product is major.

7. Many answers are possible. In most cases this will involve adding a deactivating group such as NO₂. Make sure to consider the directing effect of the new group when drawing the product.

8. (a) (CH₃)₃C⁺, the tert-butyl carbocation.

(b) The major product of this reaction is formed by attack at carbon G. The NO₂ group is a deactivator, which disfavors attack at carbon K and carbon J. A benzene ring is an ortho/para director, disfavoring attack at
carbon \( H \). Tert-butyl is a large group, and its placement will be sensitive to steric hindrance. Carbon \( I \) is more sterically hindered than carbon \( G \).

11. When the \( \text{Br} \) and \( \text{NO}_2 \) directing effects are not synergistic, the \( \text{Br} \) dominates. Review OCATSA section 23.08.

12. Tyrosine is most likely to be converted into the corresponding radical by this process. The radical produced from tyrosine enjoys resonance stabilization, whereas the radical produced from serine lacks resonance stabilization.

13. This abstraction occurs at site \( X \) instead of site \( Y \) because the product formed by abstraction from site \( X \) has resonance stabilization whereas product formed by abstraction from site \( Y \) lacks resonance stabilization.

14. If the mechanism step of question 12 is a radical chain initiation, then the majority of the remaining radical chain mechanism steps are propagation steps. Only a very tiny amount of product is formed by a radical chain step called termination.

15. Radical fate # 2 = addition to a pi bond.

Fate # 2 illustration:

Radical fate # 3 = radical combination.

Fate # 3 illustration: This is the only possible answer using the given reactants. “Fate unlikely” is also an acceptable answer in this case.

16. Dioxygen is a less reactive (aggressive) radical than hydroxyl radical. As discussed in lecture, each unpaired electron in dioxygen gains some stabilization by interacting with the other unpaired electron. Hydroxy radical lacks this stabilization.

17. Chlorine radical \( 
\text{·Cl} \) or \( \text{Cl}^\cdot \)