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. Reaction becomes faster. DMF ($\varepsilon = 37$) and methanol ($\varepsilon = 33$) have nearly equal polarity, but DMF is aprotic whereas methanol is protic. Hydrogen bonding stabilizes the nucleophile more than the transition state because the nucleophile has a full negative formal charge whereas the transition charges are partial charges. Thus a change from protic to aprotic solvent increases the reaction rate.

2. Strength of base. CH$_3$S is not strong enough for an E2 reaction, especially when the leaving group is not an excellent one. The strength of the nucleophile is irrelevant because an E2 reaction is dependent on the strength of the base and not the strength of the nucleophile.

3. An SN$_1$ reaction gives a mixture of inversion (major product) and retention (minor product). Other product answers may be possible.

4. Tow acceptable answers: Reaction becomes faster (if you assume OSO$_2$CF$_3$ is a better leaving group than iodide ion due to resonance, electronegativity, and inductive effects) or No significant change (if you recall that both iodide and triflate are in the excellent leaving groups category).

5. Strength of nucleophile, steric effects, and solvent effects. CH$_3$OH is poor nucleophile (especially in a protic solvent such as itself) which slows (but does not necessarily prevent) SN$_2$. The carbon bearing the leaving group is secondary, which also slows (but does not necessarily prevent) SN$_2$. Products C and D are both produced by the same mechanism.
8. 

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CH}_3 & \quad \text{Cl} \\
\text{CF}_3 & 
\end{align*}
\xrightarrow{\text{NaOCH}_3 \text{CH}_3\text{OH}}
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{OCH}_3 \\
\text{CH}_3 & \quad \text{C} = \text{CH}_2
\end{align*}
\]

Product E (major) + Product F

Note the lack of wedges for the groups attached to the alkene carbons in the product. Remember that alkene carbons are trigonal planar, and therefore the attachments will lie in the plan of the paper. Verify this with a model.

This product is not formed because the C–Cl and β C–H bonds of the starting alkyl chloride cannot easily become periplanar. Verify with a model.

9. 

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & 
\end{align*}
\xrightarrow{\text{CH}_3\text{OCH}_3}
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & 
\end{align*}
\]

10. Both products violate Zaitsev's rule. The Zaitsev product shown in solution 8 cannot be formed.

11. 

\[
\begin{align*}
\text{CH}_3 & \quad \text{H} \\
\text{CF}_3 & \quad \text{CH}_3 \\
\text{Cl} & 
\end{align*}
\]

Note periplanarity of C–Cl and β C–H bonds.

12. Reaction becomes slower. \(\text{CH}_3\text{CH}_2\text{OH}\) is a much poorer base than \(\text{CH}_3\text{ONa}\).

13. Steric hindrance and solvent effects. The carbon bearing the leaving group is 3°, which prevents \(S_N2\). The solvent is protic; this reduces nucleophilicity.

14. 

\[
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{Cl} \\
\text{CH}_3 & 
\end{align*}
\xrightarrow{1:1 \text{H}_2\text{O}/\text{CH}_3\text{OH}}
\begin{align*}
\text{CH}_3 & \quad \text{CF}_3 \\
\text{CF}_3 & \quad \text{OCH}_3 \\
\text{CH}_3 & \quad \text{C} = \text{CH}_2
\end{align*}
\]

Product G + Product H

The reaction produces this alkene less than products G and H because this alkene is less stable (terminal and disubstituted).
15. Product G is produced in a greater amount than product H, because product G has a tetrasubstituted alkene whereas the alkene of product H is only trisubstituted. CH$_3$OH and H$_2$O are of nearly identical basicity, so either can be used to deprotonate the carbocation intermediate.

16. The major product of the reaction shown in question 14 is product G because this product contains the most stable alkene (internal tetrasubstituted versus internal trisubstituted or terminal disubstituted in the other products).

17. Strength of base. Water and methanol are poor bases. E2 needs a strong base, especially when the leaving group is not excellent.

18. Reaction becomes faster. Changing CH$_3$ to Ph makes a more stable carbocation, which accelerates the rate-determining step. The CF$_3$ to Ph change has no significant rate effect.

19. (CH$_3$)$_3$COH. A 3° carbon is bonded to three carbon groups. Hydrogen atoms, CH$_3$O groups, and HO groups do not count towards degree of substitution. The central carbon of (CH$_3$)$_4$C has four attached carbon groups, and is called a quaternary carbon.

20. (a) Errors: The product has one extra carbon. An E2 reaction with tert-butoxide as the base gives the less substituted alkene as the major product. Changes: Remove extra carbon in products. Give correct product ratio, or change base to one that follows Zaitsev’s rule.

Corrected reaction:

\[
\text{Br} \quad \xrightarrow{\text{K}^+ \text{-OC(CH$_3$)$_3$}} \quad \text{CH$_3$O} \quad + \quad \text{HOCH$_3$} \\
\text{Major product} \quad \text{Minor product}
\]

(b) Error: In an S$_1$N$_1$ reaction, the major product is formed by the capture of the predominant nucleophile. Changes: Change iodide in product to OH, because water (not iodide) is the predominant nucleophile.

Corrected reaction:

\[
\text{Cl} \quad \xrightarrow{\text{NaI}} \quad \text{OH} \\
\text{Cl} \quad \text{H$_2$O} \\
\text{OH}
\]

21. S$_1$N$_1$ and E1. The two humps in both cases are carbocation formation and a carbocation fate. An S$_2$2 or E2 reaction usually has just one hump, but can have two if (for example) the nucleophile is deprotonated before attacking the carbon bearing the leaving group.

22. CH$_3$OH and water. Review meaning of aprotic solvent and the structures of DMF and acetone at the Illustrated Glossary of Organic Chemistry.

23. (b) Tertiary carbocation rearranges to primary carbocation. All of the choices given are possible carbocation fates, but only this one is unlikely.

24. (a) CH$_3$O$. CF$_3$CH$_2$O$ suffers from an electron-withdrawing inductive effect. CH$_3$OH lacks a negative formal charge. PhO$ suffers from resonance delocalization of its formal charge.

(b) CH$_3$O$. The leaving group ability of CH$_3$S is enhanced by sulfur's larger atomic radius. CH$_3$OH loses a formal charge when it departs. CF$_3$CH$_2$O$ is assisted by an electron-withdrawing inductive effect.

(c) CH$_3$CH$_2$OCH$_2$CH$_3$. This solvent has the lowest polar bond to nonpolar bond ratio.
25. (d) \[ \text{This carbocation has the greatest number of significant resonance contributors.} \]

26. DMF. This is an aprotic "Goldilocks" solvent.

27. \( S_{\text{N2}} \). Not E2 because there is no strong base. The carbon bearing the leaving group is secondary. The leaving group is moderate. Iodide ion in acetone is a good nucleophile. The \( S_{\text{N2}} \) conditions are met.

28. All S. \( S_{\text{N2}} \) gives 100% inversion.

29. \( S_{\text{N1}} \). When subjected to aqueous solvolysis, there is no strong base or good nucleophile, so E2 and \( S_{\text{N2}} \) cannot happen. The solvent is highly polar, the leaving group moderate, and the carbocation intermediate secondary, so the \( S_{\text{N1}} \) conditions are met. E1 occurs simultaneously with \( S_{\text{N1}} \), but E1 gives an elimination product, not a solvolysis product.

30. Mostly S, some R. \( S_{\text{N1}} \) reactions give a mixture of inversion and retention, with inversion being the major product.