1. (a) 

Iodide is on a $3^\circ$ carbon is therefore too sterically hindered to be replaced in an $S_N2$ reaction. In a protic solvent, $\text{CH}_3\text{S}^-$ is a stronger nucleophile than $\text{CH}_3\text{O}^-$. 

(b) 

Solvolyis via the more stable carbocation intermediate.

(c) 

The strongest base present removes the hydrogen $\beta$ and periplanar to the carbon-chlorine bond.

2. Several answer are possible. Perhaps the most obvious is to switch the leaving groups:

3. (a) Slower. $\text{PhS}^-$ is a poorer nucleophile due to resonance.

   (b) No change. The change is irrelevant because the leaving group is still chloride ion.

4. (a) Methanol. A charged solute is more stable in a more polar solvent.

   (b) Equal. The stability of a neutral solute is essentially solvent-independent.

   (c) Methanol. A solute with partial charges is more stable in a more polar solvent.

5. 

The acetone energy profile curve is constructed based on answers 4(a)–(c). The stabilization change is greater for the reactants than the transition state because one of the reactants has a full formal charge whereas the transition state has only partial charges.
6. (a) CH\textsubscript{3}OH
(b) CH\textsubscript{3}OH

7. Energy profile B. Reaction 1(b) is a three-step \textit{S\textsubscript{N}1} reaction, in which the first step is the rate-determining step (has the largest $\Delta G^\ddagger$).

8. (a) Slower. CH\textsubscript{3}OH is more polar than (CH\textsubscript{3})\textsubscript{3}COH.
(b) Faster. The carbocation intermediate derived from the reactant with OCH\textsubscript{3} is more stable than the carbocation derived from the reactant without OCH\textsubscript{3}, because the former carbocation has more resonance contributors (including a contributor having a full valence shell on each atom).

9. (a) Slower. Water is a weaker base than methoxide ion.
(b) Faster. The $\beta$ H–C bond is now periplanar to the carbon-iodine bond. Iodide is a better leaving group than chloride.

10. A (the \textit{S\textsubscript{N}2} reaction) and C (the E2 reaction).

11. (a) E2. The C–LG and $\beta$ C–H bonds must be periplanar for E2 to occur.
(b) \textit{S\textsubscript{N}1}. \textit{S\textsubscript{N}1} favors R\textsubscript{3}–LG because this leads to a tertiary (or maybe even tertiary with resonance) carbocation. R\textsubscript{3}–LG prevents \textit{S\textsubscript{N}2} due to steric hindrance. E2 has no requirement for degree of substitution at the carbon bearing the leaving group.
(c) E2 (or none). By definition \textit{S\textsubscript{N}1} involves at least two steps. \textit{S\textsubscript{N}2} might include deprotonation of the nucleophile before the actual substitution step. We haven't seen any examples of nonconcerted E2 reactions in Chem 14D.

12. Molecule E. The leaving group in molecule F lacks the CF\textsubscript{3} electron-withdrawing inductive effect. The benzene ring in molecule G is not in a position to assist via resonance. (Work out the resonance contributors if you don't see this.) The molecule H leaving group ($\text{-OCF}_3$) lacks the resonance effects of the other leaving groups.

13. \begin{tabular}{c|c|c}
<table>
<thead>
<tr>
<th>(a) \textit{S\textsubscript{N}2}:</th>
<th>Major Product</th>
<th>Another Significant Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3\text{C}$</td>
<td>$\text{H}_3\text{C}$</td>
<td>$\text{X}$</td>
</tr>
<tr>
<td>$\text{H}^\text{H}\text{C}$</td>
<td>$\text{H}_3\text{C}$</td>
<td>$\text{Ph}$</td>
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<tr>
<td>$\text{H}^\text{H}\text{C}$</td>
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<td>$\text{Ph}$</td>
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</table>

\textit{S\textsubscript{N}2} gives inversion only. HO$^-$ is a better nucleophile than CH\textsubscript{3}OH.

(b) \textit{S\textsubscript{N}1}:

\begin{tabular}{c|c|c}
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<td>$\text{Ph}$</td>
</tr>
</tbody>
</table>

\textit{S\textsubscript{N}1} solvolysis gives a mixture of inversion and retention products, with the inversion product being major. A carbocation captures the most prevalent nucleophile mostly; this is not necessarily the best nucleophile present.

$S_N1$: Transition state A. This is the only unimolecular transition state choice. It has the correct configuration. Verify with a model.

15. (b) Antibonding orbital. $S_N2$ backside attack and subsequent inversion of configuration occurs because the nucleophile attacks the carbon lobe of the C-LG bond antibonding orbital.

16. (a) Solvolysis, (b) inversion, (c) retention, and (e) accelerated by resonance (in the leaving group and/or carbocation intermediate).

17. A transition state is the highest energy structure along the reaction profile reaction coordinate (or x-axis) for every mechanism step.

18. $X = N(CH_3)_2$: The nitrogen lone pair provides resonance stabilization. Nitrogen is less electronegative than oxygen or fluorine, and therefore nitrogen is a better resonance donor than oxygen or fluorine.

19. Capture a nucleophile: 

Be deprotonated; form pi bond:

Rearrange:


Rate-determining step: The mechanism step having the greatest activation energy or $\Delta G^\ddagger$ (i.e., the slowest step) and therefore the step that has the greatest influence on reaction rate.

Leaving group: An atom or group which breaks away from the rest of the molecule taking with it the pair of electrons which used to be the bond between the leaving group and rest of the molecule.

Protic solvent: A solvent that is also a hydrogen bond donor.

Polar solvent: A solvent whose dielectric constant ($\varepsilon$) is 20 or more.

Elimination reaction: A reaction in which a molecule loses atoms or groups of atoms, usually from adjacent atoms, almost always resulting in a new pi bond.

Zaitsev's rule: The major product of a dehydrohalogenation elimination reaction is the more highly substituted alkene.