

Statistics: High score, average, and low score will be posted on the course web site after exam grading is complete. The exam is ready to be picked up when these numbers are posted.

Some questions have more than one answer, even though only one answer is listed here.

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

1. (b) ...is mostly *S*, rarely *R*

(f) ...cannot be determined is also acceptable. Consider a case where an  $S_N2$  reaction destroys a stereocenter because the nucleophile is the same as one of the existing attachments to the carbon that is undergoing substitution.

2.  $\sigma^*$  orbital

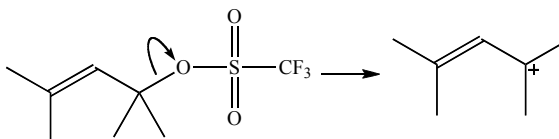
3. Steric hindrance *caused by the leaving group after its departure but incomplete migration away from the carbocation.*

4. Polar, aprotic, an amide

5.  $\text{CH}_3\text{CH}_2\text{O}^-$

6.  $\text{CF}_3\text{SO}_3^-$

7. Many answers are possible, for example:



8. If  $S_N2$  and  $S_N1$  rates both increase, write 'increase.' If  $S_N2$  and  $S_N1$  rates both decrease, write 'decrease.' If  $S_N2$  and  $S_N1$  rates are both unchanged, write 'unchanged.' Otherwise write 'cannot determine.'

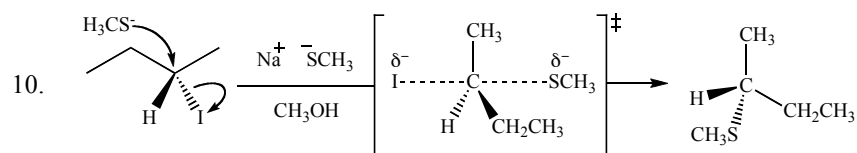
(a) Increases

(b) Cannot determine *Increases for  $S_N2$  but no change for  $S_N1$ .*

(c) Cannot determine *Depends on if the  $E_{act}$  increase is for the rds or another step.*

(d) Cannot determine *Depends upon the reactants and mechanism: most  $S_N2$  reactions slow down as  $\epsilon$  increases, but in some  $S_N2$  reactions the rate increases with higher  $\epsilon$ .*

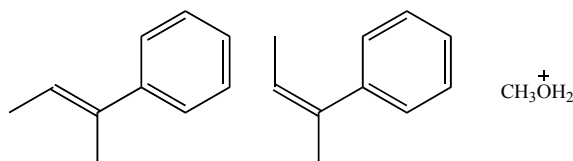
9.  $\text{CH}_3\text{CH}_2\text{OH}$   $\epsilon = 25$ ,  $(\text{CH}_3)_3\text{COH}$   $\epsilon = 11$ , and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$   $\epsilon = 20$ . *Increasing number of nonpolar bonds (C-H and C-C) causes decrease in  $\epsilon$ .*



11. Product **B**

*When a molecule has a stereocenter but the absolute configuration is not specified with solid and broken wedges, a mixture of stereoisomers (enantiomers or diastereomers) is implied.*

12. There are a few reasonable answers, such as:

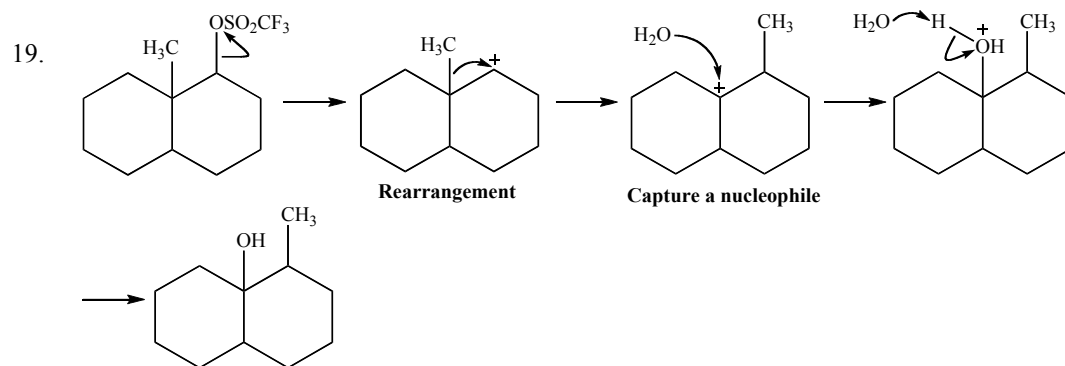


Normally we don't consider inorganic materials such as NaCl to be important products of organic reactions. Note that the question does not require products derived from the  $S_N1$  mechanism, even though this is the dominant mechanism in this reaction.

13.  $\Gamma^-$   $Cl^-$  forms stronger hydrogen bonds than  $I^-$ , and therefore is a poorer nucleophile in a protic solvent such as  $CH_3OH$ .  $Na^+$  is a cation and therefore not a nucleophile.  $CH_3O^-$  isn't even present, so its nucleophilicity is a moot point.
14. The principle reason why iodide ion is a good nucleophile is its low electronegativity. 'Poor hydrogen bonding' is not an acceptable answer. When present, hydrogen bonding decreases nucleophilicity, but its absence does not increase nucleophilicity. Metaphor: just because you are out of debt doesn't automatically mean you are wealthy.
15. The principle reason why this reaction occurs by the  $S_N1$  mechanism is steric hindrance prevents  $S_N2$  when the leaving group is bonded to a tertiary carbon.
16. (b)  $CH_3I$  and NaF in  $CH_3OH$  Fluoride ion hydrogen bonding is so strong that fluoride ion's nucleophilicity is shut down in a protic solvent.
17. Slowest reaction: (d)  $(CH_3)_3CCl$  and NaCl in  $CH_3CH_2OH$ . Product of slowest reaction:  $(CH_3)_3COCH_2CH_3$ .  $Cl^-$  is a poorer leaving group than  $I^-$ .  $CH_3CH_2OH$  is the least polar solvent choice.  $(CH_3)_3CCl$  is identical in all aspects to the reactant, so it is not a product.

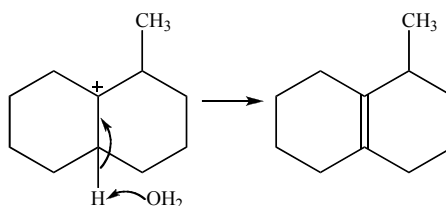


Any other cases have lower degree of substitution at the carbocation carbon, or less resonance. This answer also has ring strain, but the destabilization caused by ring strain is outweighed by the extra stability gained by aromaticity. Some answers without aromatic structures may also have been accepted for partial or full credit.

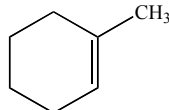


The final deprotonation occurs with  $H_2O$  instead of  $CF_3SO_3^-$  because water is a stronger base than  $CF_3SO_3^-$ .

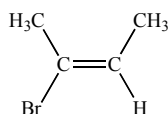
20. Third fate: Be deprotonated to form a pi bond:



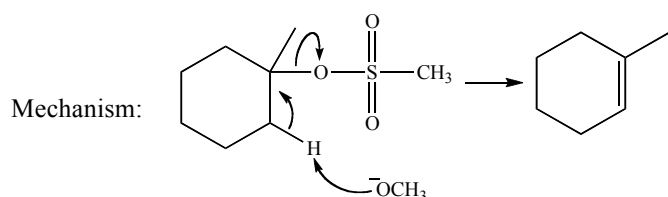
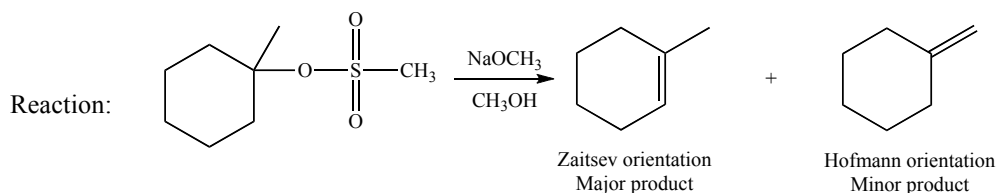
21. The internal, trisubstituted alkene is most stable:



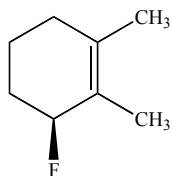
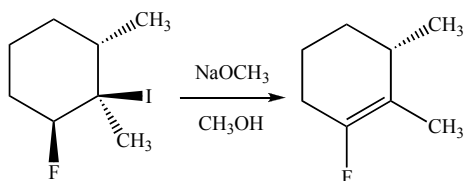
22. That the alkene is *cis* requires two carbon groups on the same side of the alkene. That the alkene is *E* requires the highest Cahn-Ingold-Prelog priority group on each alkene carbon to be on opposite sides. This can only be achieved by using one group whose priority is higher than carbon, such as bromine. Numerous answers are possible, for example:



23. Many examples are possible, but in order to clearly illustrate Zaitsev's Rule, the starting material must also be capable of providing a Hofmann product under the right conditions. For example:

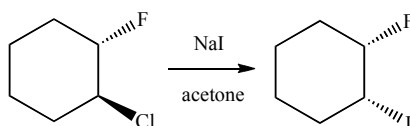


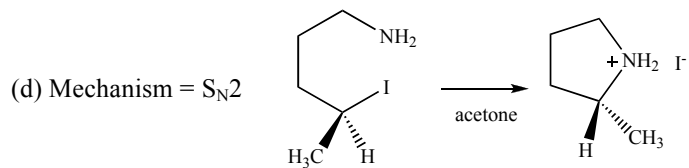
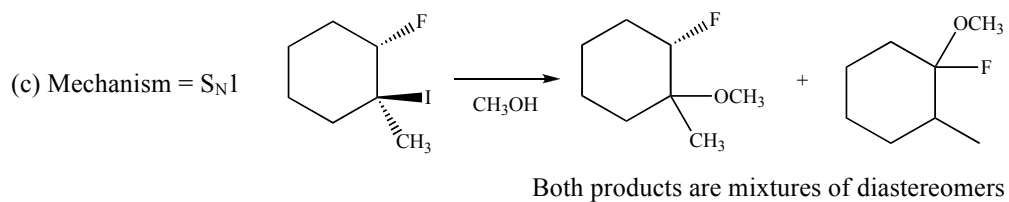
24. (a) Mechanism = E2



is not formed because the C-H bond next to the methyl group cannot become coplanar with the C-I bond.

(b) Mechanism = S<sub>N</sub>2





25. Leaving group: Portion of the molecule that departs along with the pair of electrons that was the bond between the leaving group and some other atom.