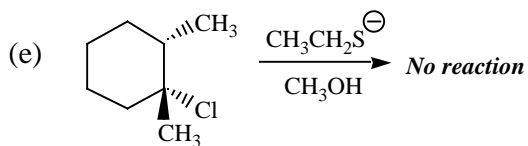


(b) The reaction is concerted.

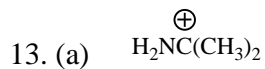
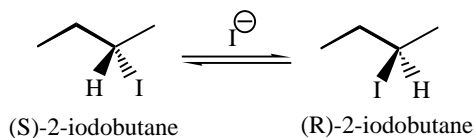
(c) If  $\text{CH}_3\text{CH}_2\text{S}^-$  is replaced with  $\text{CF}_3\text{CH}_2\text{S}^-$  the reaction **becomes slower**.

(d) If  $\text{CH}_3\text{OH}$  is replaced with DMF the reaction becomes **faster**.

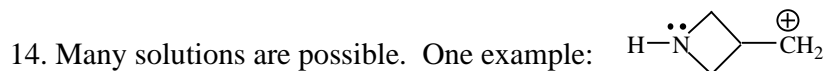


*A reaction rate of zero is less than any other rate!*

12. Recall that  $\text{S}_{\text{N}}2$  substitution occurs with inversion of stereochemistry. Reaction of (S)-2-iodobutane with iodide ion forms (R)-2-iodobutane and another iodide ion (the leaving group). This (R) product can react with iodide ion again, forming the (S) enantiomer. Since the (R) and (S) enantiomers have the same stability, they will be present in a 1:1 mixture (racemic) when equilibrium is reached.

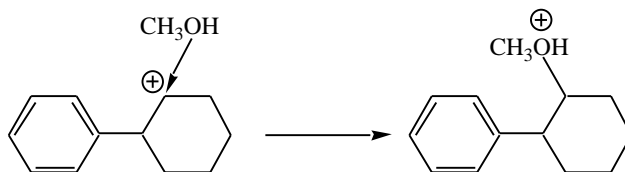


(b) (2 point) The most stable carbocation is **2°** and **resonance-stabilized**.

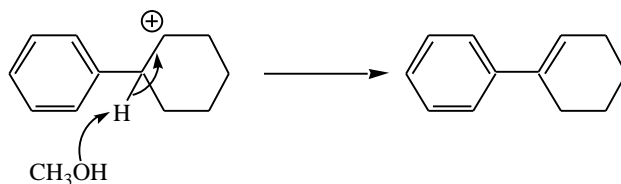


15. (a) The fundamental driving force that controls all carbocation fates is the desire to become more stable by filling the open octet on carbon and obtaining a neutral formal charge.

(b) Fate #1: **Capture a nucleophile**



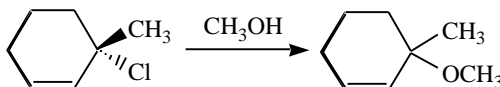
Fate #2: **Lose proton; form  $\pi$  bond**



Fate #3: **Rearrange**



Consider this reaction:



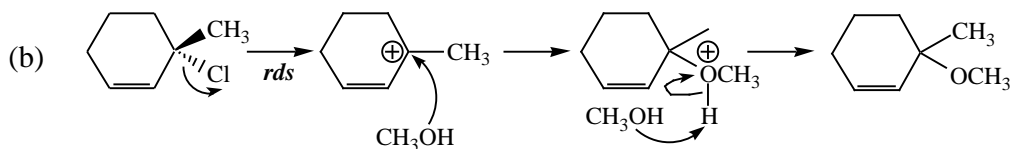
16. (a) When choosing between  $S_N2$  and  $S_N1$ , we consider  $S_N2$  first because it generally has lower activation energy for the rate-determining step and is thus the faster reaction. For a substitution reaction to proceed by the  $S_N2$  mechanism, it must meet certain requirements:

- Moderate or better nucleophile:  $\text{CH}_3\text{OH}$  is a poor nucleophile.
- Moderate or better leaving group:  $\text{Cl}^-$  is a moderate leaving group.
- Not  $3^\circ$ : The carbon at which the substitution occurs is  $3^\circ$ .

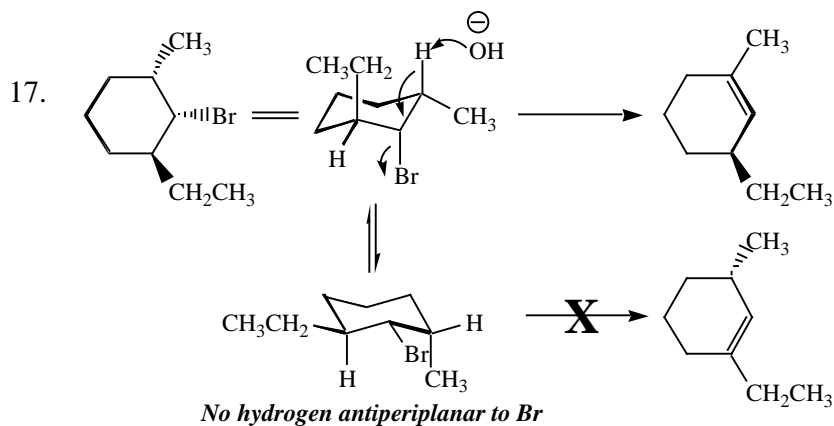
Two of the three  $S_N2$  requirements are not met, so  $S_N2$  is not a reasonable mechanism choice. The requirements for an  $S_N1$  mechanism are:

- Moderate or better leaving group:  $\text{Cl}^-$  is a moderate leaving group.
- Carbocation more stable than  $1^\circ$ : The carbocation is  $3^\circ$  with resonance.
- Polar solvent:  $\text{CH}_3\text{OH}$  is polar ( $\epsilon = 33$ ).

The  $S_N1$  requirements are clearly met, so the most probable mechanism for this reaction is  $S_N1$ .

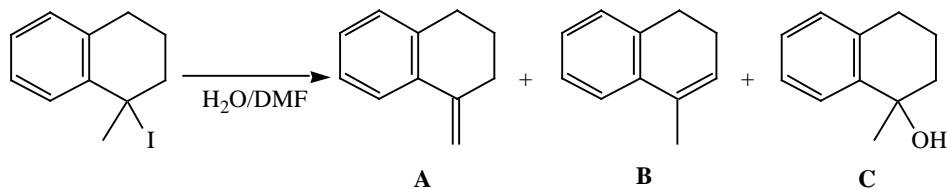


(c) The reaction product is a **mixture of (R) and (S) enantiomers**.



The product with the double bond bearing the ethyl group cannot be formed because the cyclohexyl hydrogen next to the ethyl group is never antiperiplanar to the leaving group.

Reaction of the iodide shown below with water and DMF produces three products:



18. (a) The product predicted by Zaitsev's rule is **B**.

(b) The mechanisms that best account for the products are **E1** (products **A** and **B**) and  $S_N1$  (product **C**).

(c) When choosing between substitution and elimination mechanisms, we consider the concerted mechanisms ( $E2$  and  $S_N2$ ) first because these generally have lower activation energy for the rate-determining step than the carbocation mechanisms ( $S_N1$ ,  $E1$ ). Furthermore we consider  $E2$  before  $S_N2$ , except in the case of primary alkyl halides.

E2 requires a strong base (usually  $\text{RO}^-$  or  $\text{R}_2\text{N}^-$ ). The absence of a strong base suggests this reaction cannot proceed by the E2 mechanism.

$\text{S}_{\text{N}}2$  requires that the carbon at which the substitution occurs cannot be tertiary. The iodide in this case is tertiary, so the  $\text{S}_{\text{N}}2$  mechanism is prevented.

This leaves  $\text{S}_{\text{N}}1$  and E1. These reactions have the same rate-determining step, and thus they occur with roughly equal ease. They also have the same requirements:

- Moderate or better leaving group:  $\text{I}^-$  is an excellent leaving group.
- Carbocation more stable than  $1^\circ$ : The carbocation is  $3^\circ$  with resonance.
- Polar solvent: Water ( $\epsilon = 80$ ) and DMF ( $\epsilon = 37$ ) are both polar.

Since the  $\text{S}_{\text{N}}1$  and E1 requirements are met we predict the reaction will give a mixture of  $\text{S}_{\text{N}}1$  and E1 products.