

ELIMINATION REACTIONS: E2 and E1

Chem 14D
Winter 2006

Credit to Professor Steven Hardinger's Chemistry 14D Thinkbook (Winter 2006, blue version) and Paula Bruice's Organic Chemistry (4th edition) from which information, diagrams, and examples for this project were used.

In an **Elimination Reaction** (in particular, a E_2 elimination),

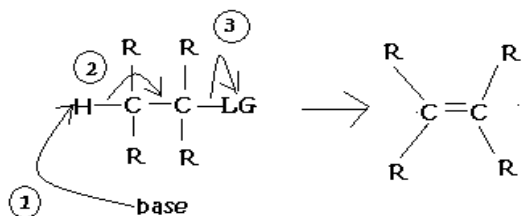
- an atom or group of atoms (**leaving group**) is removed from a carbon
 - while a proton (βH^+) is removed from an adjacent carbon.
- } • A **double bond** consequently forms between the two carbons.

Thus, in an elimination reaction, a **C=C pi bond is formed**.

i.e. $\text{C-C } sp^3$ (alkane) \rightarrow $\text{C=C } sp^2$ (alkene) \rightarrow $\text{C}\equiv\text{C } sp$ (alkyne)

E2 Mechanism

General:



1. Base takes away H^+ from (i.e. **deprotonates**) the carbon that is adjacent to the carbon attached to the leaving group
2. The pair of electrons from the C-H bond move to occupy the p orbital between the H-C-C-LG. A **pi bond is formed**.
3. **Leaving group leaves**.

Kinetics:

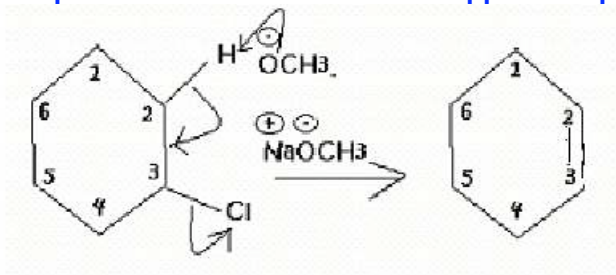
- Notice Steps 1–3 occur in one step. The E2 mechanism is **concerted**. No intermediates are formed.
- Also, formation of the product with a C=C pi bond depends on both the concentration of both reactants: $\text{R}_3\text{C-LG}$ and base.

Thus, the rate law for E2 can be written:

$$\text{Rate} = k[\text{R}_3\text{C-LG}][\text{base}]$$

- The rate law depends on the first order concentration of two reactants, making it a 2nd order (**bimolecular**) elimination reaction and giving us the **2** in E2.

Example from Thinkbook Lecture Supplement pg. 8



Step 1: DEPROTONATION OF β -HYDROGEN.

OCH_3^- is a strong base. It deprotonates by taking the β -H from Carbon 2.

Step 2: FORMATION OF $\text{C}=\text{C}$ PI BOND.

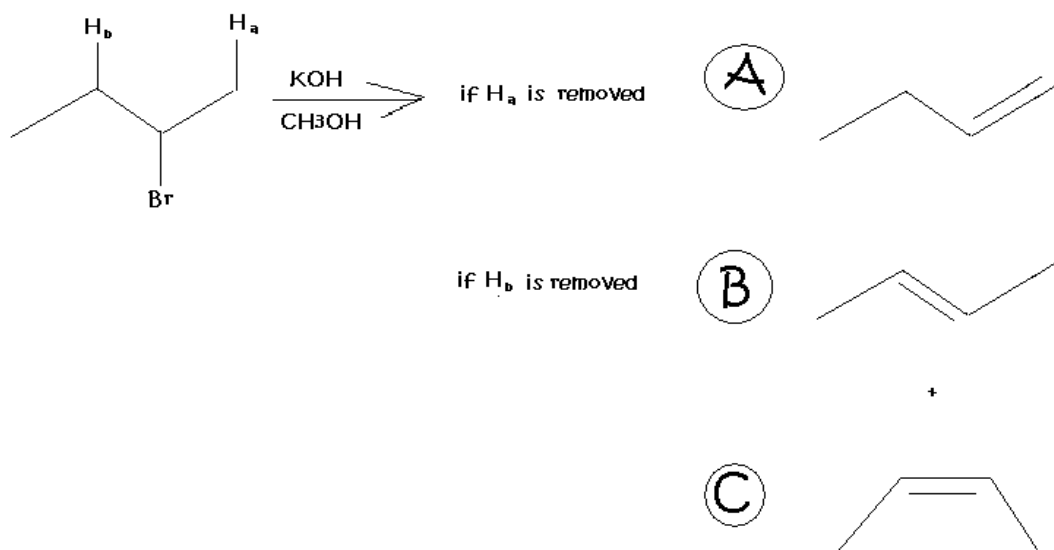
The electrons from the C-H bond form a pi bond between C2 (the β carbon) and C3 (α carbon).

Step 3: LEAVING GROUP LEAVES.

Cl^- , the leaving group, is ejected from C3.

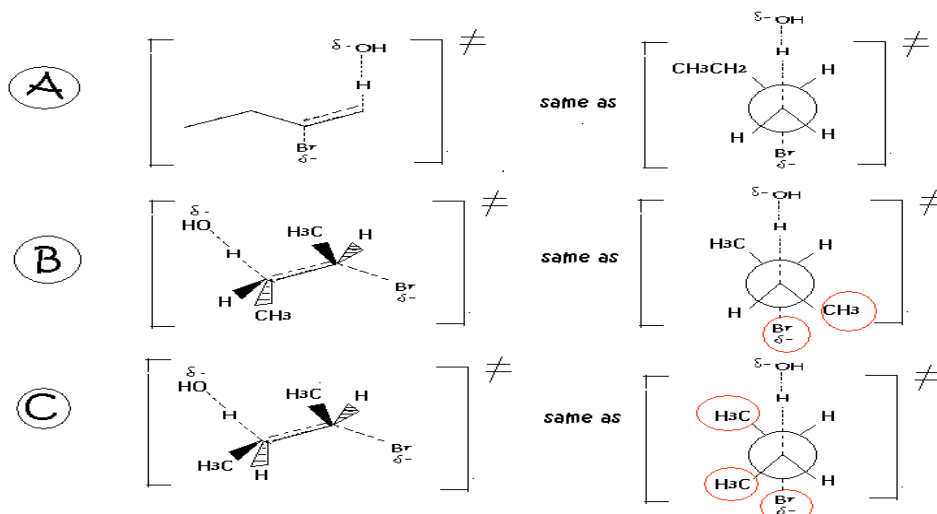
- Note: β -H could have also been taken from C4. However, in this case the cyclohexane is symmetrical, so the product would have been identical to the one provided.
- In other cases, when α -carbon is asymmetrical, elimination of β -hydrogens from different adjacent carbons adjacent to the C-LG will result in the formation of multiple products. In such instances, we must consider factors of **stability**.

Using Example from Lecture Supplement pg. 8



First, let us consider **Torsional Strain** of the Transition State [TS][‡]

We can use **Newman projections** to determine which transition state of these three products is most stable, and therefore which subsequent product is most likely to form.



Transition States A – C are listed in order of increasing torsional strain due to van der Waals interactions. The groups of atoms highlighted in red show us potential energetically expensive overlapping positions.

From this demonstration, we are able to visualize an important requirement for the E2 mechanism...

Observation #1: E2 products favor antiperiplanar arrangement of H-C, C-LG bonds.

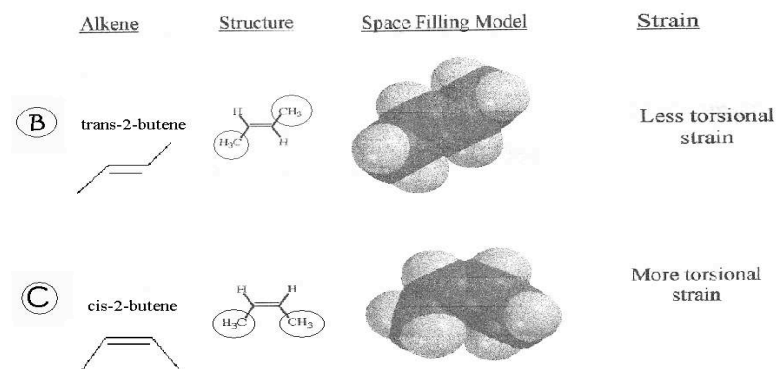
Anti – to reduce torsional strain, minimize van der Waals interactions

Periplanar – so that p orbitals can overlap to form the pi bond

Second, because transition state exhibits qualities of both the reactants and products, we must also consider **Torsional Strain** of the Products (in particular, the alkene).

For this, we can use space filling models to show the differences in torsional strain of substituents in both cis and trans conformation.

Lecture Supplement pg. 10



Cis and trans apply only when there are two carbon substituents on opposite ends of an alkene.

Cis means the two substituents are on the **same** side of the chain.

Trans means the substituents are on **opposite** sides of the chain.

From this diagram, it is evident that when substituents are arranged in a cis conformation torsional strain increases and stability decreases. Since E2 reactions generally favor the most stable product, the cis-alkene is typically not the favored product. This brings us to our second conclusion about product stability...

Observation #2: Trans alkene is more stable than cis alkene.

Third. In our previous analysis, we looked at alkene stability based on the positions of carbon groups attached to the alkene. Now we will take a look at the position of the alkene itself on the carbon chain.

Lecture supplement pg. 10



By empirical observation, we find that...

Observation #3: Internal alkene is generally more stable than terminal alkene.

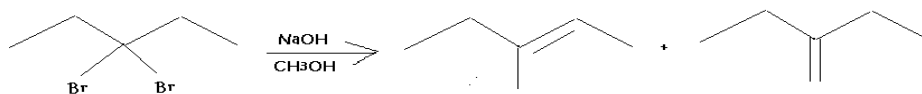
Thinkbook Practice Problem 15

For the reaction shown below:

(a) Select the major product.

(b) Write the mechanism for the major product of this reaction.

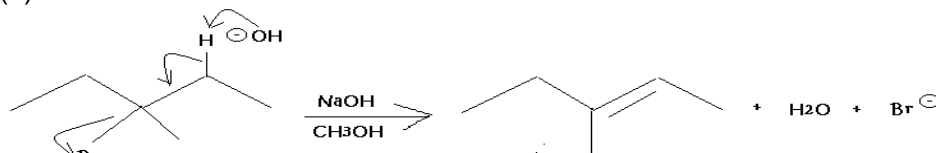
(c) Very briefly explain your choice for the reaction mechanism.



Solution:

(a) The first alkene is more substituted, and is therefore the major product.

(b)



(c) The internal alkene is favored because it is the most stable product.

Fourth, we want to see how the number of substituents (**degree of substitution**) on the alkene affects its overall stability.

We know that sp^2 bonds are stronger, and therefore more stable, than sp^3 bonds. Thus, it follows that the more sp^2 bonds a molecule has, the more likely it is to be the major product.

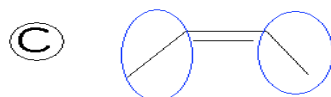


The sp^2 bonds are circled in blue.



A has only 1 sp^2 alkyl substituent, so in this analysis it is the least stable.

B has 2 sp^2 alkyl substituents, so it is more stable.



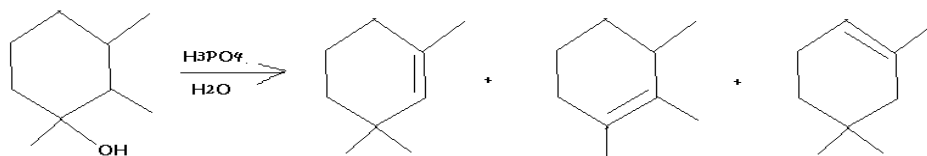
C also has 2 sp^2 alkyl substituents, even though its stability is decreased by torsional strain.

So we have our fourth conclusion about alkene stability...

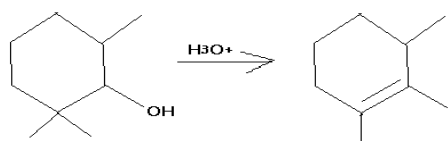
Observation #4: Alkene isomer with more sp^2 (C=C) bonds is more stable.

From Thinkbook Practice Problem 10

Pick the most stable product. Explain.



Solution:



This product has 4 alkyl groups attached to either side of the the alkene.

Things to remember...

- When strong acid is in aqueous solution (in water), consider it as H_3O^+ in the mechanism.
- Don't forget about rearrangement!

We have now covered the major factors of transition state and alkene stability pertinent to elimination reactions. However, we have one more factor to consider...

If you recall, when we consider stability of carbocations, resonance and degree of substitution are competing factors. Similarly, alkenes have two major competing factors of stability: **number of alkyl substituents** and **torsional strain**.

In general, we can observe that...

Degree of substitution outweighs torsional strain unless torsional strain is severe.

A good way to summarize the product predictions made by the above factors is **Zaitsev's Rule**, which states...

Major product of elimination is the more substituted alkene.

As stated before, when we do reactions, we want to obtain the most stable product. By favoring alkenes with electron donating carbon group substituents, Zaitsev's rule helps us predict the most stable (i.e. major) product.

However, when the **base is large** or **LG is large** (NR_3 , SR_2 , or F^-) the product is an exception to Zaitsev's Rule. That is, it follows **Hofmann Orientation**, which states...

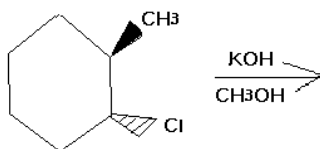
The less substituted alkene is the major product.

Or in other words, **the major product is not the more substituted alkene.**

Thinkbook Practice Problem 17

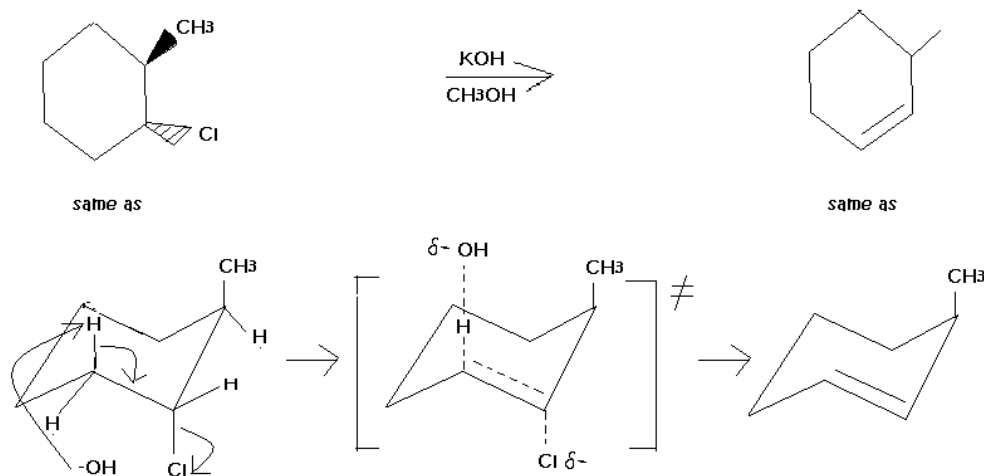
For the reaction shown below:

(a) Provide a curved arrow mechanism, including all transition states, showing how the major product is formed.



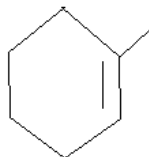
Solution:

When stereochemistry is involved, use **chair conformation** for cyclohexanes. (Remember: *draw dashes down*.)



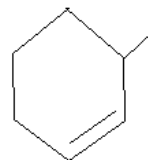
In this cyclohexane (the reactant), there are **two** β -hydrogen options:

1) the H that shares the C attached to CH_3 , which would produce



This product corresponds to Zaitsev's rule, because the most substituted alkene is produced. However, to form this cyclohexane, the β -hydrogen used was not diaxial to the LG, therefore is not the major product.

2) the two H's attached to the second β -carbon which gives us



This product does not correspond with Zaitsev's rule. It's not Hofmann's orientation either because neither the base nor the LG is large. However, **the less substituted product is major** because a diaxial β -H was available to form a pi bond.

If the leaving group is not in an axial position to begin with...

- Do a **chair flip**. Then look for axial β -hydrogens.
- This will guide you to **diaxial** leaving group and β -hydrogen(s), if any are present.
- By looking for LG and β -H in diaxial positions, you will achieve a H-C-C-LG that is **antiperiplanar**.

We are now ready to summarize the **E2 Requirements**:

- 1) **Strong base**
- 2) **Moderate or better leaving group**
- 3) **β -Hydrogen (H-C-C-LG) in antiperiplanar arrangement.**

Requirements 1 and 2 (base and leaving group) interact with one another, which means that if you have a really strong base, you can get away with a moderately weaker leaving group, and vice versa. The third requirement, for the sake of β -eliminations, is non-negotiable.

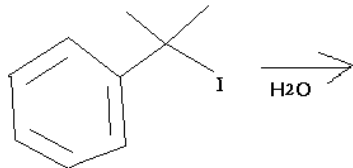
E1 Mechanism

Looking at the requirements for the E2 mechanism, the base and leaving group requirements are somewhat flexible. However, if **the leaving group is poor**, E2 probably won't occur no matter how strong your base is. Conversely, **if the base is weak**, E2 still wouldn't occur because the mechanism is no longer concerted. As long as a β -hydrogen is present, you can still have an Elimination Reaction, only we will call this mechanism **E1**.

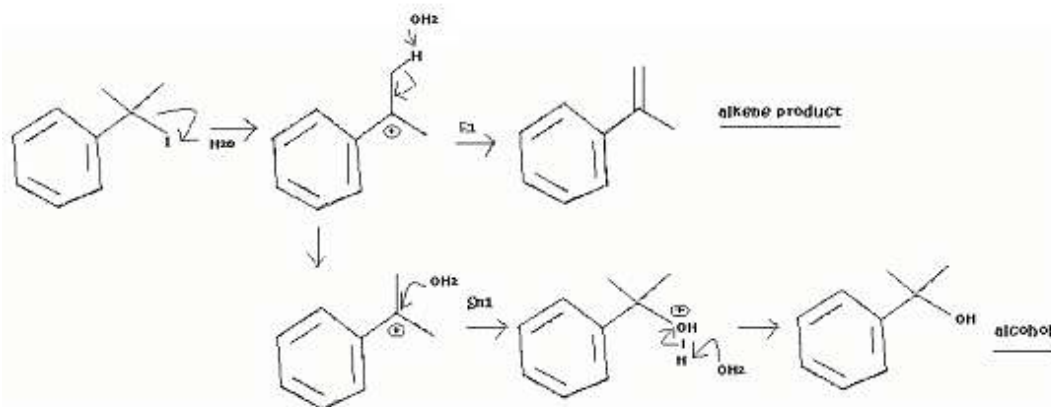
E1 stands for...	Implication...	Comparable to...
Elimination	A β -hydrogen will be eliminated, and a pi bond will form between two carbons.	E2 Product (pi bond formation)
Unimolecular	Rate is determined by the leaving group leaving and a carbocation forming.	$\text{S}_{\text{N}}1$ Requirements (carbocation intermediate)

Example Mechanism from Thinkbook Practice Problem 20(c)

Draw the curved arrow mechanism and major product(s).



Solution:



Reason for multiple products:

Carbocation Mantra: “Whenever we see a carbocation in a mechanism step regardless of where it comes from, we first consider **resonance**.” Resonance helps us determine how stable a carbocation is, and thus how likely it is to form. The carbocation above is tertiary and is located next to an adjacent pi bond from the benzene ring, so we can say it is tertiary with resonance, making it a relatively very stable carbocation.

Next we consider the **3 fates** of a carbocation. 1) Rearrangement is possible if it leads to more stable carbocation. 2) If the carbocation captures a nucleophile, the reaction will proceed by the S_N1 mechanism. 3) The carbocation can also lose a proton to form a pi bond, proceeding by the E1 mechanism.

Note, each of the three fates is equally weighed by a carbocation, and because a carbocation is “desperate but not fussy,” it will often under go more than one of these fates in any given reaction.

Also note, because S_N1 and E1 mechanisms both concern the formation of a carbocation intermediate, a reaction that involves a carbocation will often undergo **both** S_N1 and E1 simultaneously.

Therefore, the alkene product of the previous problem is the result of an elimination reaction (E1), while the alcohol is produced from substitution (S_N1).

Kinetics:

The formation of a carbocation involves losing a bond (R₃C-LG) without gaining any bonds, so we consider it the rate determining step. Therefore, the rate law of E1 is written as:

$$\text{Rate} = k[\text{R}_3\text{C-LG}]$$

E1 Requirements:

- 1) Stable carbocation (1° w/ resonance or better)
- 2) Moderate or better leaving group
- 3) Polar solvent
- 4) β -Hydrogen (H-C-C-LG)

Finally, between Elimination and Substitution mechanisms, how can we predict which is most likely to occur?

Order of preference

- E2
- S_N2
- E1/S_N1

Requirements

- 1) Strong base
 - 2) Moderate or better leaving group
 - 3) Antiperiplanar H-C-C-LG
- 1) Not 3° R₃C-LG
 - 2) Moderate or better leaving group
 - 3) Moderate or better nucleophile
 - 4) Polar (aprotic) solvent
- 1) Stable carbocation (1° w/ res or better)
 - 2) Moderate or better leaving group
 - 3) Polar (protic) solvent
 - 4) β -hydrogen (for E1)

Strategy:

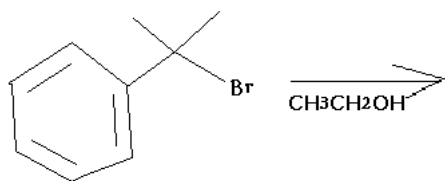
When approaching a reaction in which the mechanism(s) is not specified, it may be helpful to think of the mechanism requirements and order of preference as a "checklist." If a requirement of a higher priority mechanism (example, E2) is not met, cross it off the list and move on to the next mechanism (S_N2). Again, if a requirement for this mechanism is not met, we are only left with the two (equally) lower ranking mechanisms, E1 and S_N1. Because both E1 and S_N1 share the same rate determining step, it is generally safe to presume that both mechanisms occur simultaneously.

Last Example...

Thinkbook Practice Problem 18

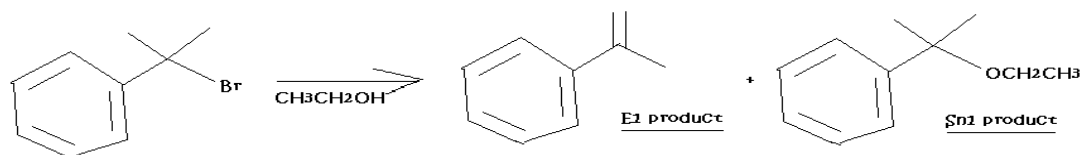
For the reaction shown below:

- Write all the products of this reaction.
- Provide a mechanism that clearly shows how all of your products are formed.
- For each reaction mechanism listed, give a single, brief reason why it was not chosen for this reaction: S_N1, E1, S_N2 and E2.

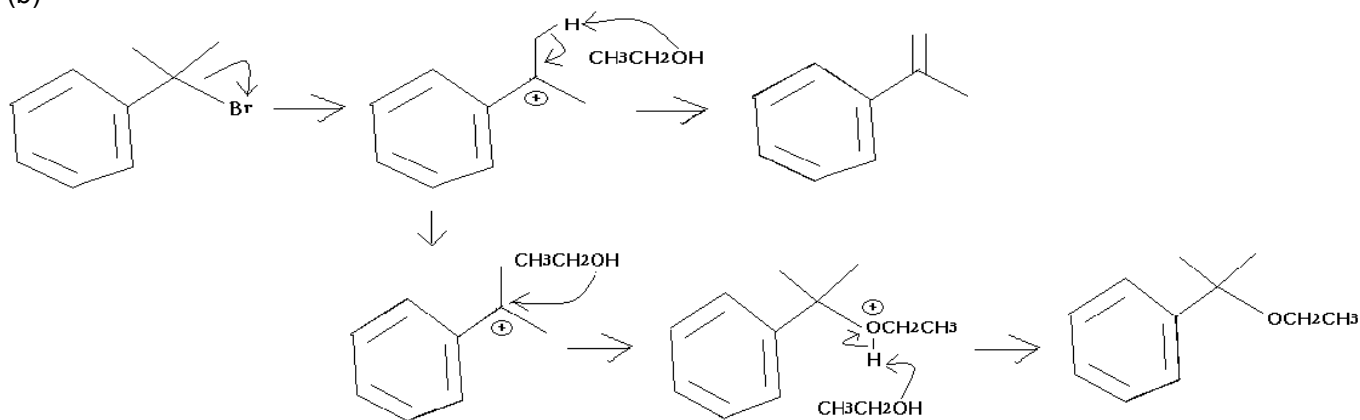


Solution:

(a) We predict the products to be from E1 and S_N1. (See part (c) for details.)



(b)



(c) In order of preference,

E2: Ethanol (CH₃CH₂OH) is a poor base. Bromide is not a good enough leaving group to overcome this poor basicity, so E2 is ruled out.

S_N2: Ethanol is a poor nucleophile. Bromide is not a good enough leaving group to overcome this poor nucleophilicity. More obviously, the carbon bearing the leaving group is 3°!

E1 and S_N1: Not ruled out. The carbocation to be formed is relatively stable (3°), a moderate or better leaving group (bromide) is present, and the reaction occurs in a polar, protic solvent. And for E1, there is also a β-hydrogen adjacent to the carbon bearing the leaving group.