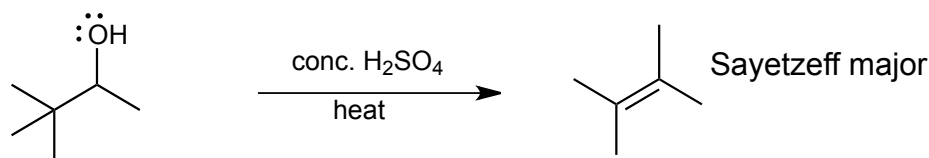


9 Water as a Leaving Groups

- By now we KNOW that -OH can be a good leaving group if it is protonated, **water is a good leaving group**
- This works for substitution (SN1 and SN2), and we should not be surprised if we can also do eliminations
- Again, the reactions start by protonating the -OH of an alcohol to form a good leaving group, and then standard E1 and/or E2 mechanisms after that

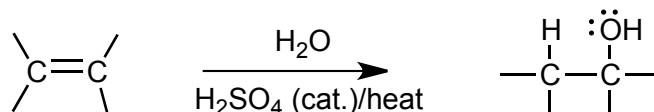
Example Problem: Give the product AND Mechanism for the following elimination reaction.



- Sulfuric acid protonates the -OH in a Bronsted acid/base reaction to convert the -OH into a good leaving group
- Water is such a good leaving group that the elimination is almost always **E1 with 3° and 2° alcohols**
- Water is such a good leaving group that E1 occurs even at a secondary carbon to make a secondary cation
- **carbocation intermediates mean rearrangements!** (that hasn't changed, of course)
- the conjugate base anion of the sulfuric acid, the bisulfate anion, is the most likely base to deprotonate the carbocation intermediate, thus regenerating the acid catalyst
- The alkene formed will be the Saytzeff (Zaitsev), there are no stereochemical constraints in the E1 mechanism and the most stable alkene will form.

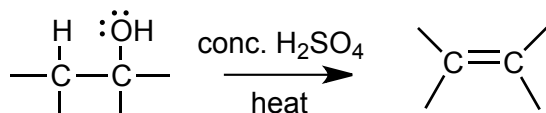
Why does the alcohol make an alkene + water when previously we learned that water + alkene gives an alcohol?

- THIS is what we learned previously



- The addition reaction "goes" because the weaker pi-bond is converted into a stronger sigma-bond
- The reagents/conditions have a **LARGE quantity of water** and a **SMALL quantity of sulfuric acid**

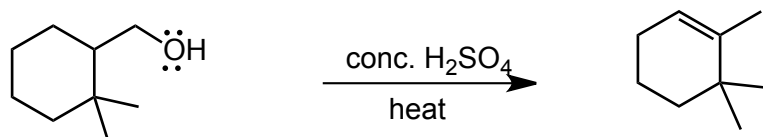
- THIS is what we now learned



- The reagents have **ZERO water** and a **HIGH concentration of sulfuric acid** (opposite of previous reaction)
- The elimination reaction "goes" because the water is highly solvated in the concentrated sulfuric acid

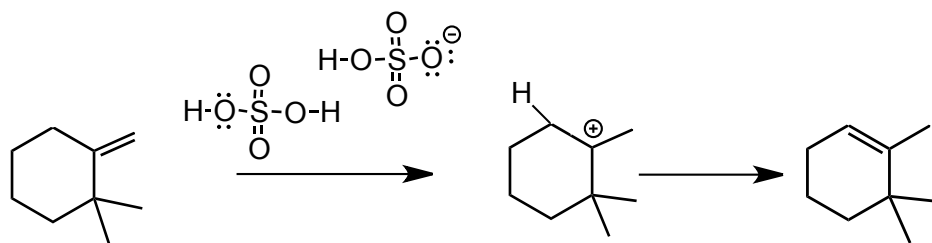
- note a special kind of **SOLVENT EFFECT** here! In an aqueous medium, acid catalyzes water ADDITION to the alkene to make an alcohol. In conc. sulfuric acid medium, the acid helps to REMOVE water from an alcohol to make an alkene (the sulfuric acid DEHYDRATES the alcohol)
- Alternate reagents and conditions are H₂SO₄/P₂O₅, and others....

Example: Primary (1°) Alcohols: E2 elimination (with rearrangement...)



- With a **primary alcohol** the **mechanism must be E2**, formation of a **primary carbocation CAN'T occur**
- BUT, even though the elimination does not involve a rearrangement, the final alkene product is usually the same one that would have been formed via an E1 reaction due to protonation followed by deprotonation (isomerization) of the primary alkene into a final more stable product

Look AGAIN at the second part of the mechanism, the rearrangement



- This effectively converts a less stable less substituted alkene into a more stable more substituted alkene, this is why this ISOMERIZATION reaction "goes"
- To solve the mechanism problem, **ADD SOME hydrogen atoms back to the line-angle structure**, the H atoms tell you exactly where you need to protonate and deprotonate
- in the presence of acid, PROTONATION will occur first, followed by deprotonation
- a less substituted/less stable alkene is converted into a more substituted/more stable alkene
- this is a REARRANGEMENT, the acid is only the catalyst (no atoms are overall added or subtracted)
- In a strong acid, especially with heat, protonation and deprotonation can OFTEN occur, and if this can result in formation of a more stable alkene, then the more stable alkene will form, and you should always include this step when doing acid catalyzed dehydrations of alcohols

The final product is the SAME MOST SUBSTITUTED ALKENE, whether the mechanism is E1 followed by cation rearrangement (2° and 3° alcohols) or E2 followed by protonation/deprotonation (1° alcohols)