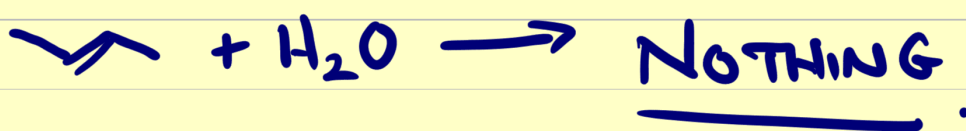


## MARKOVNIKOV'S RULE

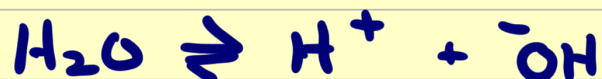
DEFN: THE POSITIVE PORTION OF THE REAGENT GOES TO THE SIDE OF MULTIPLE BOND THAT HAS THE MOST HYDROGENS

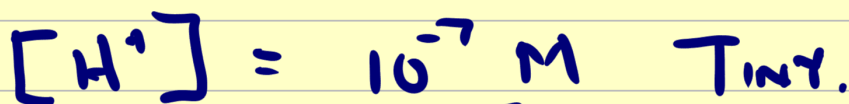
- IN SIMPLE CASES FOR  $\text{E}^+ \text{X}^-$  ADDN.  
 $\text{E}$  ENDS UP ON LESS SUBSTIT. C  
 $\text{X}$  ENDS UP ON MORE SUBSTIT. C

ADDITION OF  $\text{H}_2\text{O}$ , AND CATALYSIS.



PROBLEM  $\text{E}^+$  IS  $\text{H}^+$

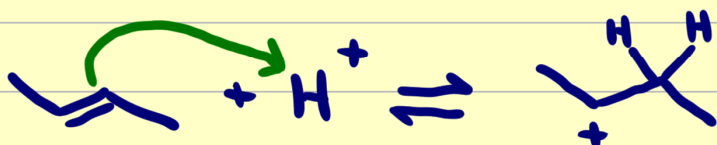




∴ TOO SLOW

- FIX THIS BY ADDING  $H^+$

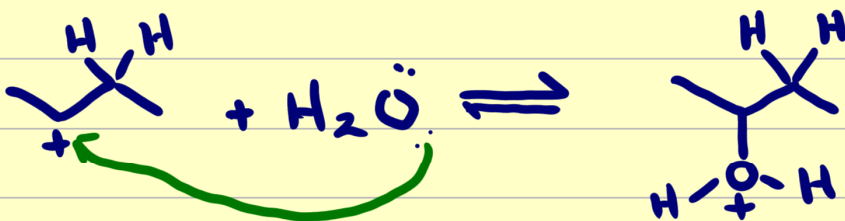
- WILL USE 10%  $H_2SO_4$  (1.9 M)



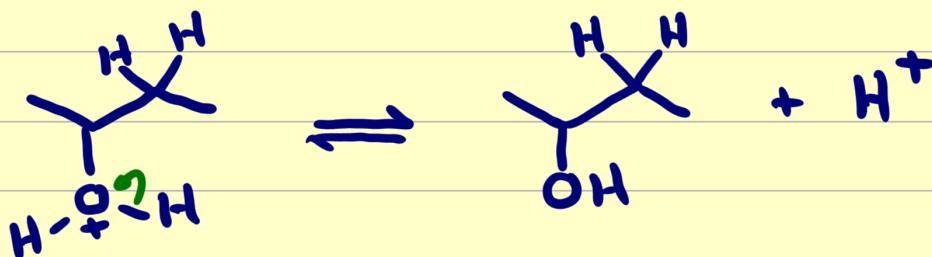
Now  $[HO^-]$  IS SMALL  $5.3 \times 10^{-15} \text{ M}$

BUT WE HAVE  $H_2O$  PRESENT

- NOT A GREAT NUCLEOPHILE, BUT GOOD ENOUGH AND IT'S '55 M



AND THEN THIS LOSES  $H^+$



## POINTS 1) $H^+$ IS A CATALYST

- SPED UP THE REACTION BY GIVING THE PROCESS A DIFFERENT, 'EASIER' MECH.

2) REGENERATED AT THE END.

WHY NOT  $HSO_4^-$  AS  $X^-$ ?

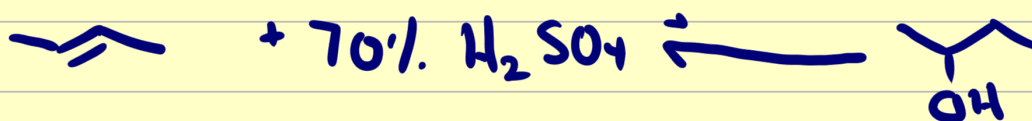
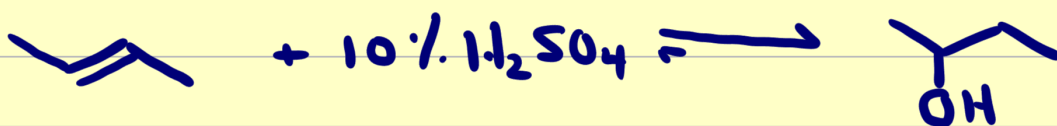
- IT'S SO STABLE THAT IT'S A POOR NUCLEOPHILE.

3) 10%  $H_2SO_4$ , NOT 70%  $H_2SO_4$

BECAUSE

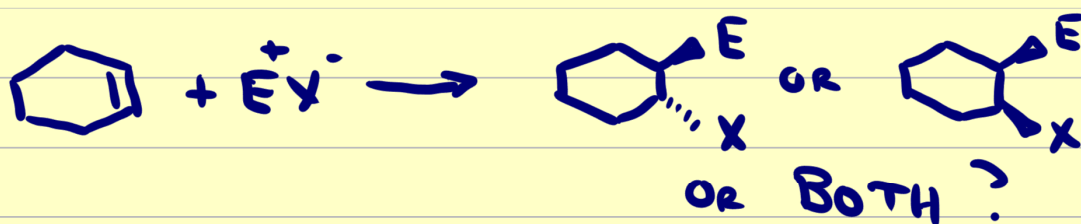


YOU'RE NUCLEOPHILE IS GONE



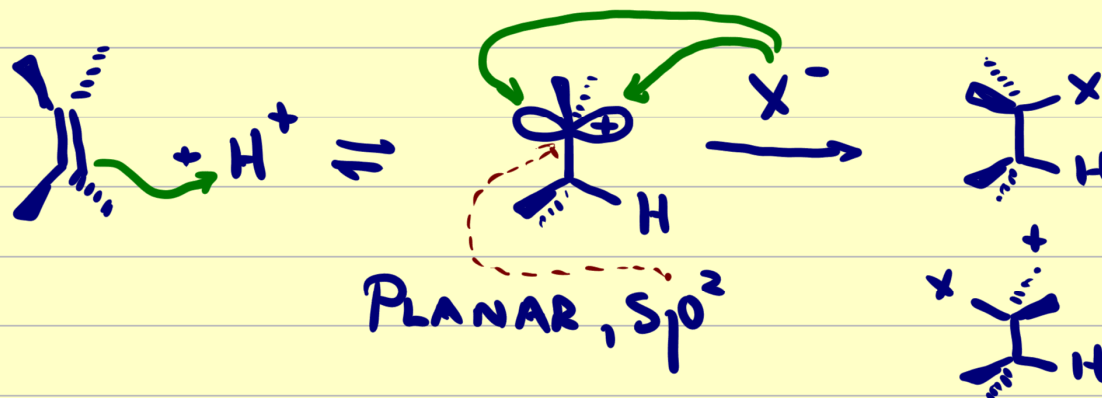
- 70%  $H_2SO_4$  DOES ELIMINATION RXN. OF THE ALCOHOL.
- SAME MECHANISM, OPPOSITE ORDER OF STEPS.
- PRINCIPLE OF MICROSCOPIC REVERSIBILITY

## STEREOCHEMISTRY OF ADDITION

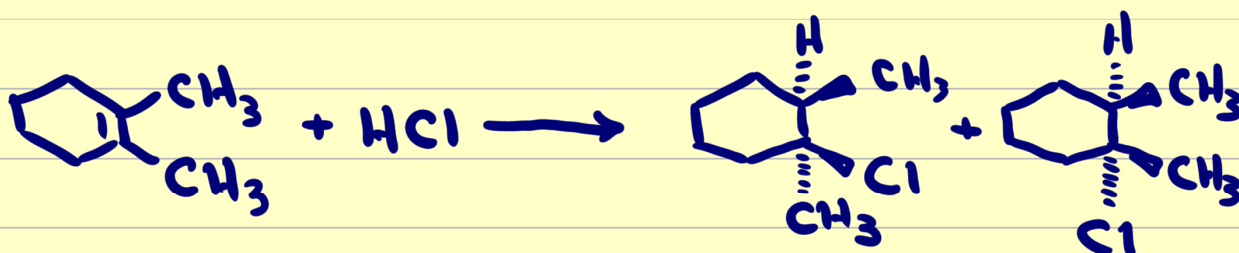


ANSWER - IT DEPENDS. - TWO SITUATIONS.

1) MOST COMMON - WHEN  $E^+ = H^+$

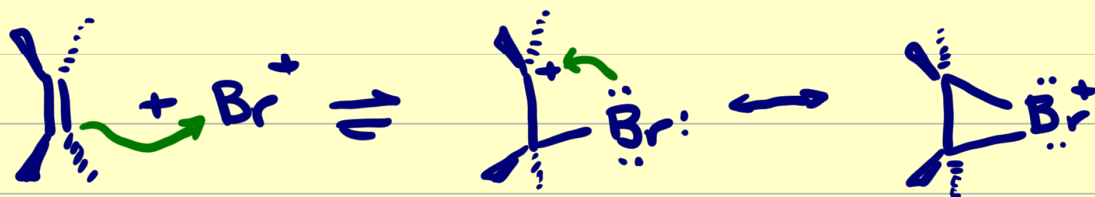


EITHER FACE OF CATIONIC CENTRE IS ACCESSIBLE - GET STEREOCHEMICAL MIXTURE OF CIS + TRANS. ADDN

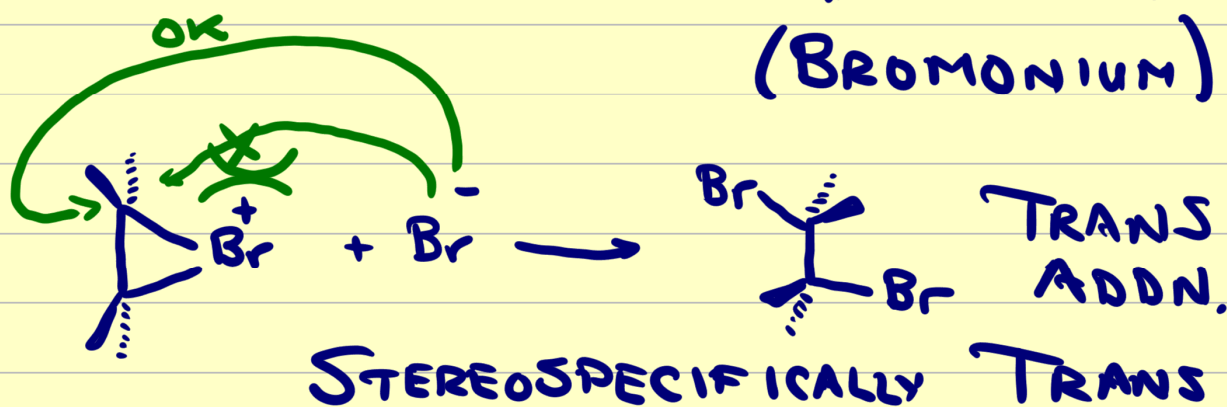


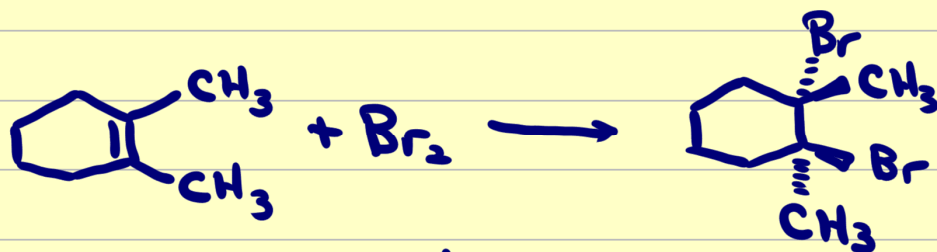
- Mix of Both.

2) IF  $E^+$  IS " $Br^+$ ", " $Cl^+$ ", " $I^+$ "  
( $Br_2$ ) , ( $Cl_2$ ) , ( $ICl$ )



HALONIUM ION  
(BROMONIUM)





- REASON -  $E^+$  HAS A LONE PAIR
- $\therefore$  CATION IS ACTUALLY CYCLIC
- $\therefore$  ONLY ONE 'FACE' OF CATION IS UNBLOCKED FOR ATTACK BY  $X^-$