(32) **Today**

7.7 Electrophilic Addition Reactions of Alkenes

7.8 Orientation of Electrophilic Additions: Markovnikov's Rule (Regioselectivity)

7.9 Carbocation Structure and Stability

7.10 The Hammond Postulate
Drawing a transition state

7.11 Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements

Next Class (33)

7.10 The Hammond Postulate
Drawing a transition state

7.11 Evidence for the Mechanism of Electrophilic Additions: Carbocation Rearrangements

(34) **Second Class from Today**

Chap 8

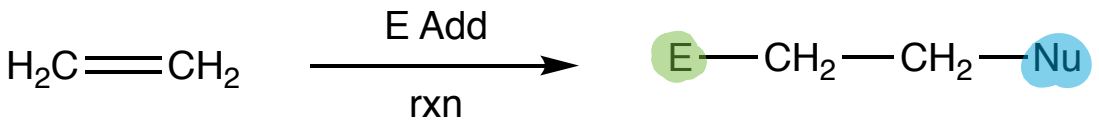
Third Class from Today (35)

Chap 8

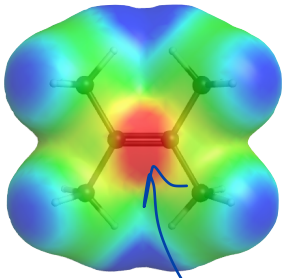
Reworked Test 3 Due Monday, December 9.

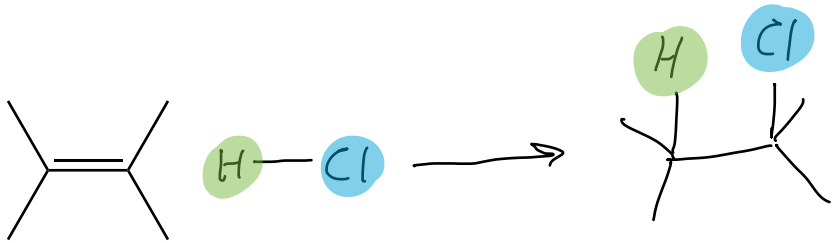
On a separate piece of paper, provide answers for any question for which you did not receive full credit. I do NOT need the test itself back.

The reactions are called electrophilic additions because the are initiated by an electrophile and two groups/atoms are added across the double bond.



E = generic electrophile Nu = generic nucleophile





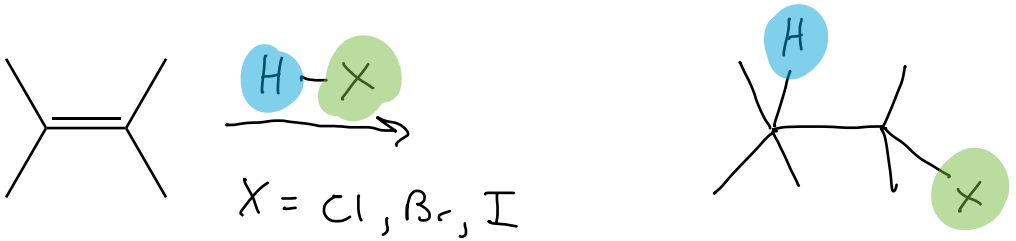
e^- rich π bond attractive to electrophiles

p orbitals overlapping to form π bond

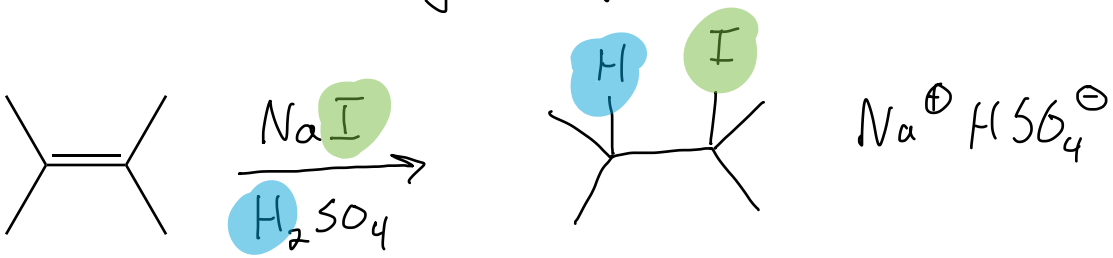
p orbitals stick out away from the nucleus

e^-'s in a π bond are much more available than e^-'s in a σ bond

H^+-based Electrophiles



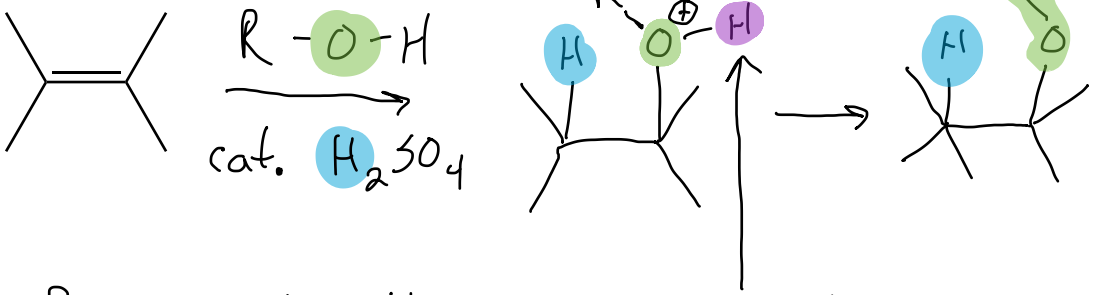
H-F is not strong enough



$Na^{\oplus}\ HSO_4^{\ominus}$

Any group 1 metal is going to be +1 when next to a nonmetal

But Na^+ is not strong acid



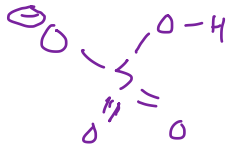
R = CH_3, etc., H

this H^+ can react with other alkenes

If R = H the alkene was converted to an alcohol.

If R = CH_3 (or other carbons) (C-O-C) ether

H_2SO_4 strong acid counter ion is not

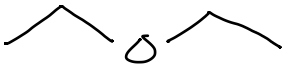


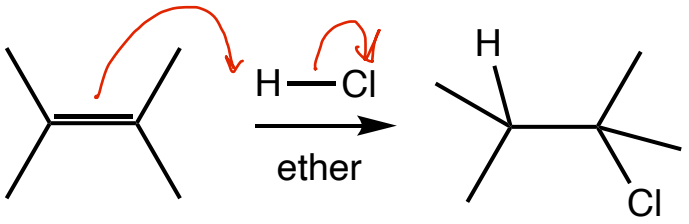
nucleophilic ... ⊖ is delocalized

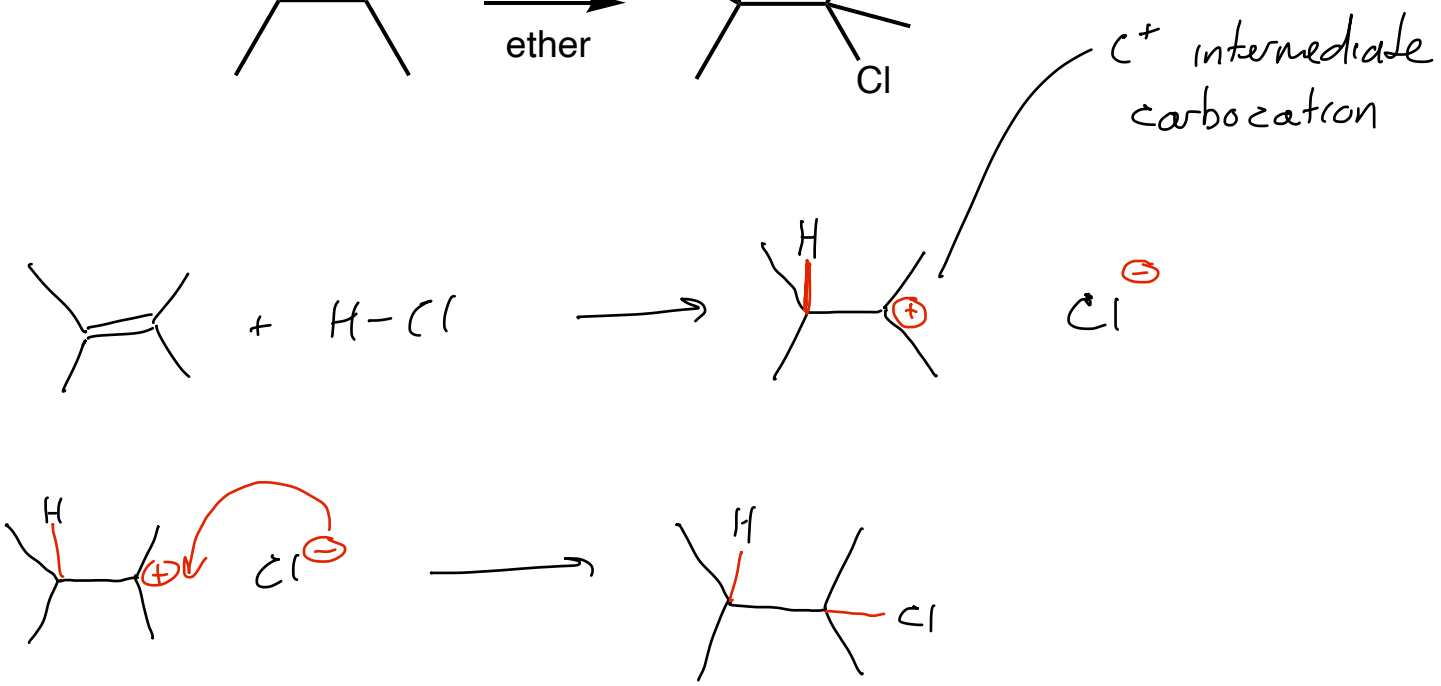
also not a strong oxidizer like HNO_3 or $HClO_3$ or $HClO_4$

Nucleophile: can the Nu be a strong base? NO

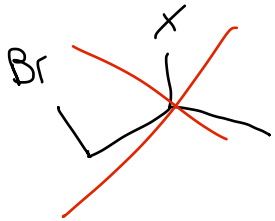
strong base will consume acid

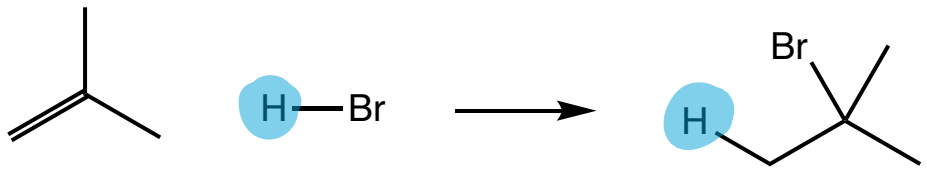


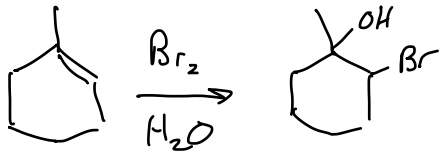

H—Cl
ether
H
Cl

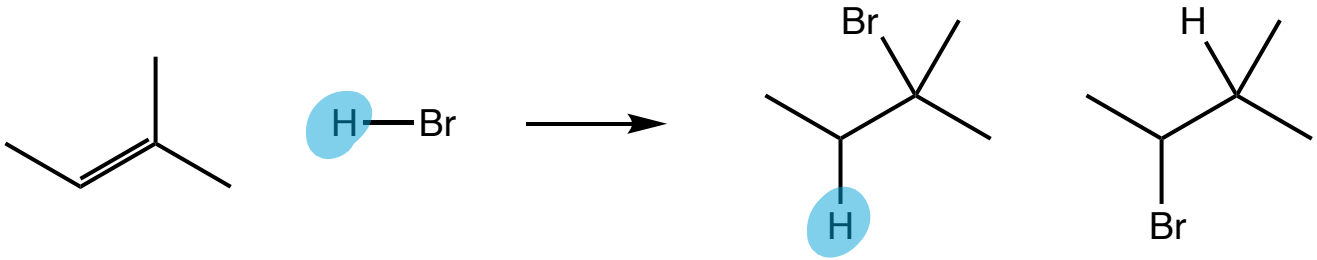

C+ intermediate
carbocation
+ H-Cl
H
Cl
H
Cl
H
Cl

Regioselectivity: The ability of a reaction to prefer the formation of one constitutional/structural isomer over another.





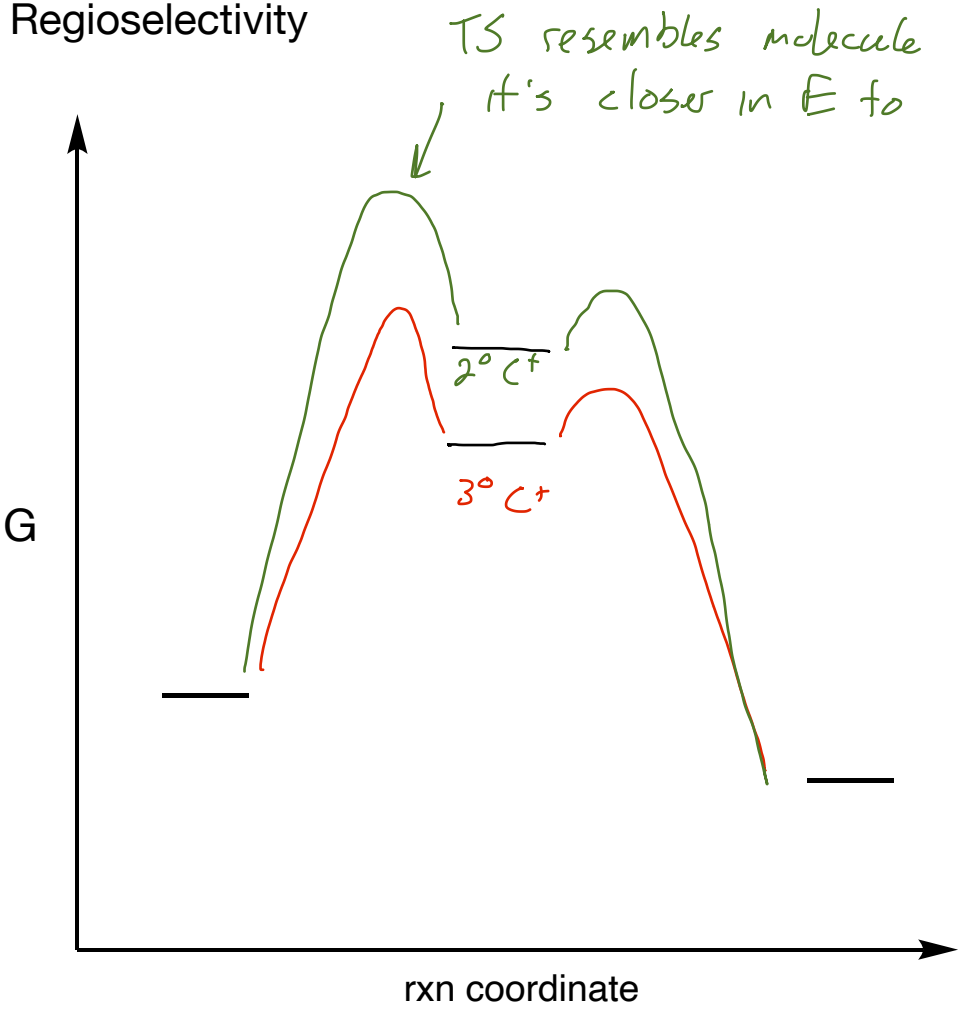


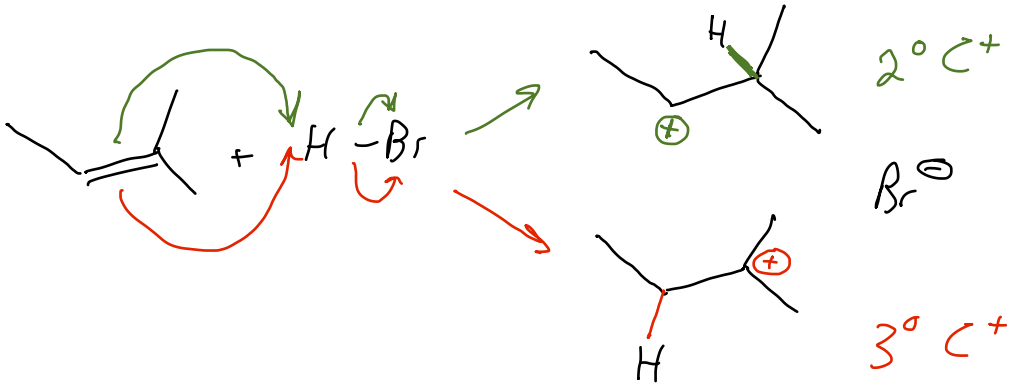


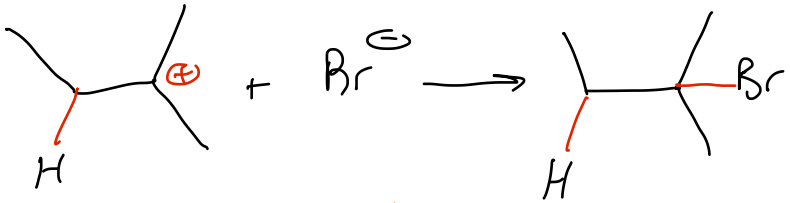
major minor

electrophile goes to the less substituted end

The Carbocation Intermediate, the Hammond Postulate and Regioselectivity

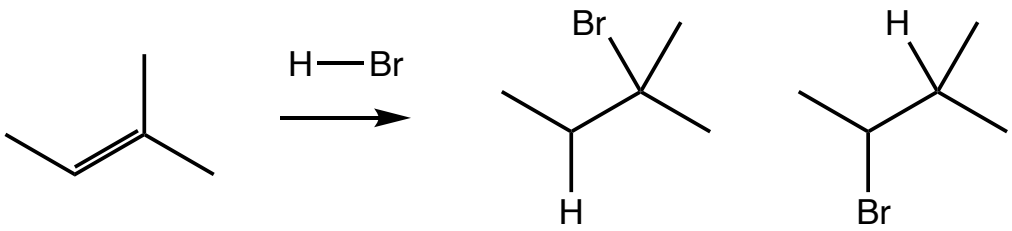






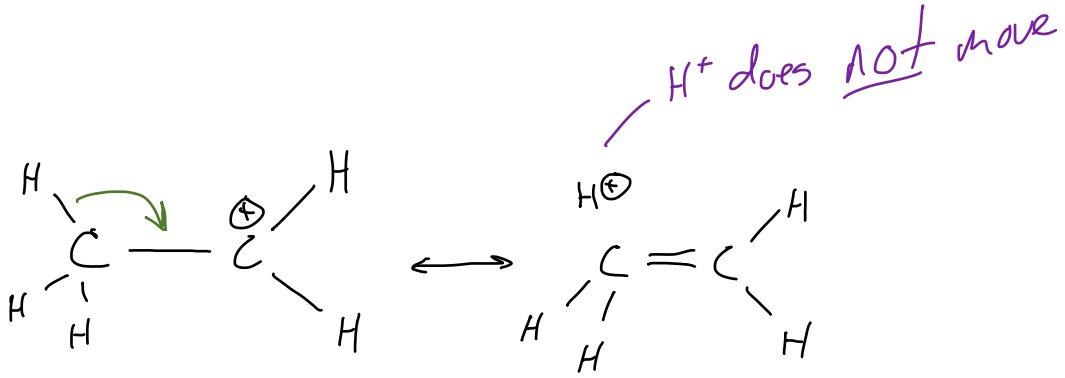
forms faster 'cuz 3° C+ is lower in E and TS is lower in E

The tiny difference (if there is one) isn't sufficient to explain the outcome

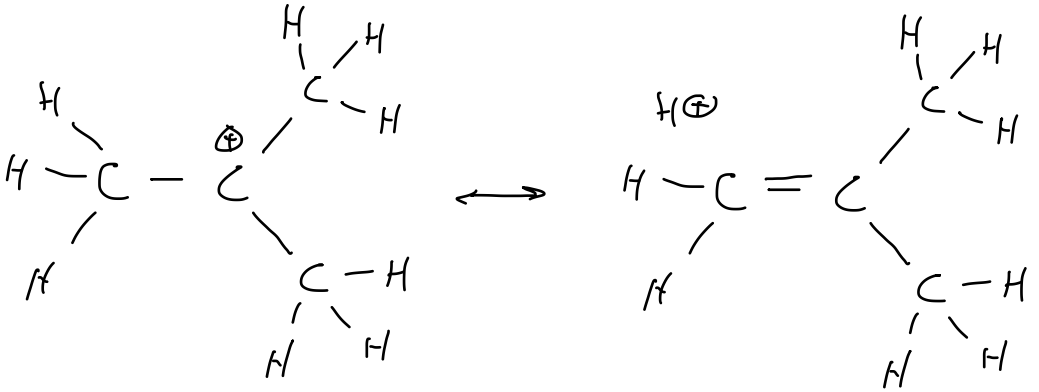


major minor

C^+ Stability



3 C-H σ bonds to help stabilize 1° C+



9 C-H σ bonds to help stabilize 3° C+

CH_3^+ < 1° C+ < 2° C+ < 3° C+

too unstable to form under typical lab conditions

https://www.westfield.ma.edu/cmasi/organic/carbocation_stabilization/carbocation-lumo-plain.html