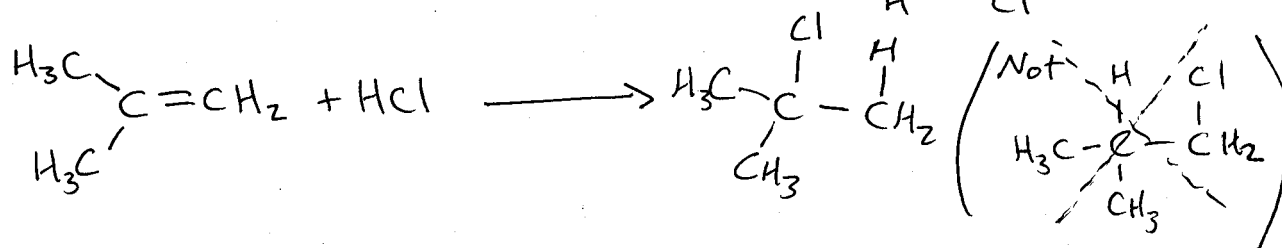
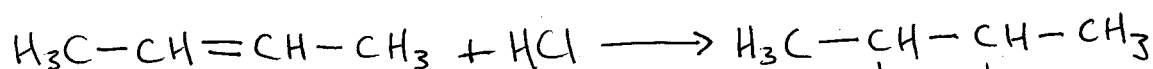
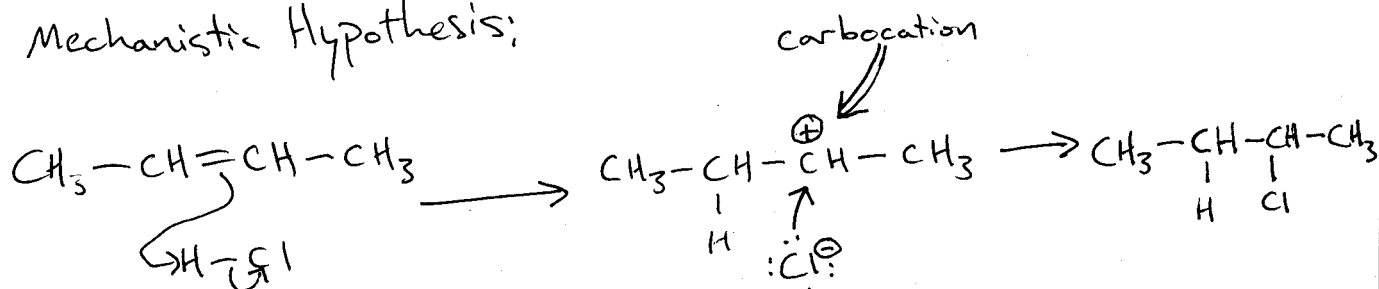


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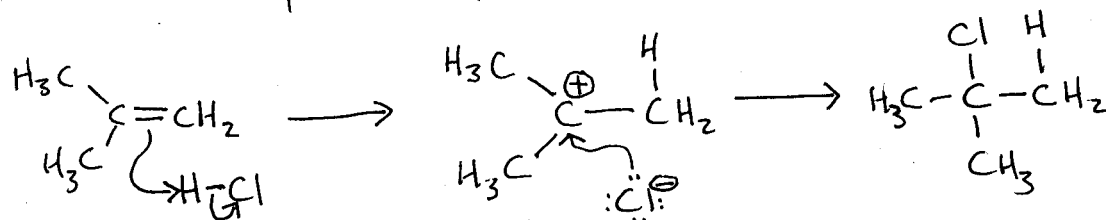
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Sites for in-class exams $\Rightarrow$ see website (Penalty for wrong room)Recall: HCl addition to alkenesLatter case: Markovnikov's Rule

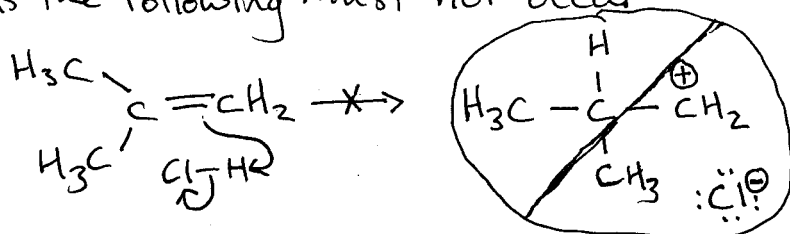
Mechanistic Hypothesis:



Extend mech. to unsymmetrical alkenes.



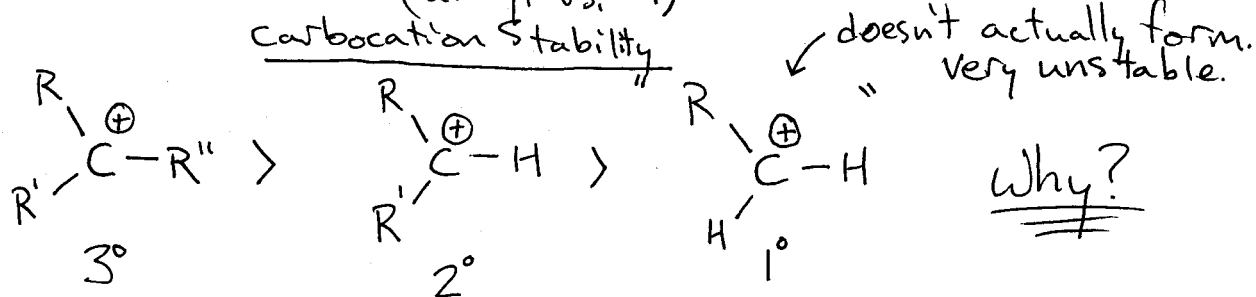
Thus the following must not occur



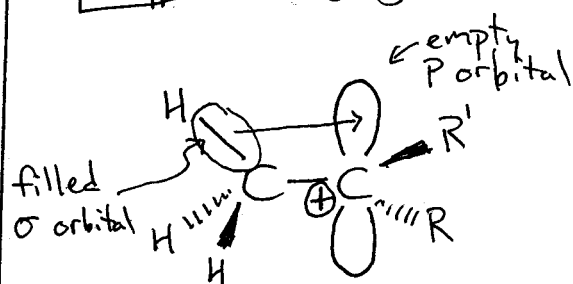
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General Conclusion from analysis of many H-X addition reactions - carbocation stability must be very sensitive to carbon substitution (alkyl vs. H)



Hyperconjugation



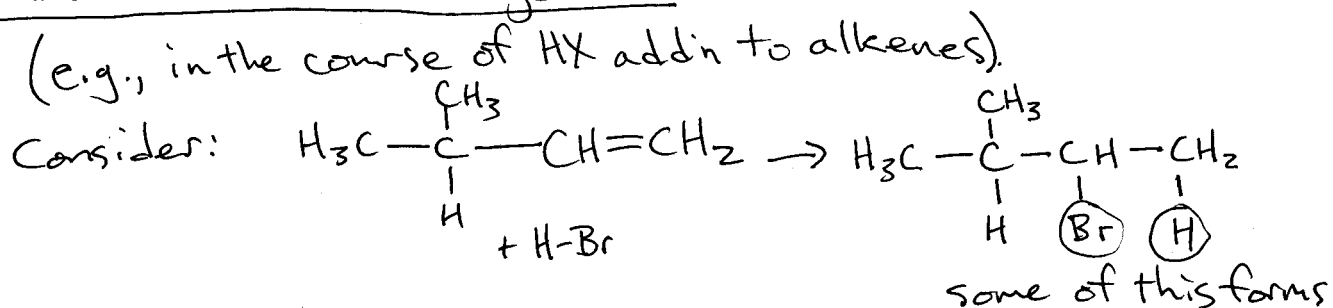
Why does an alkyl substituent stabilize a carbocation

hyperconjugation - delocalization of σ bonding electrons into adjacent empty p orbital.

- diffuses positive charge across molecule.

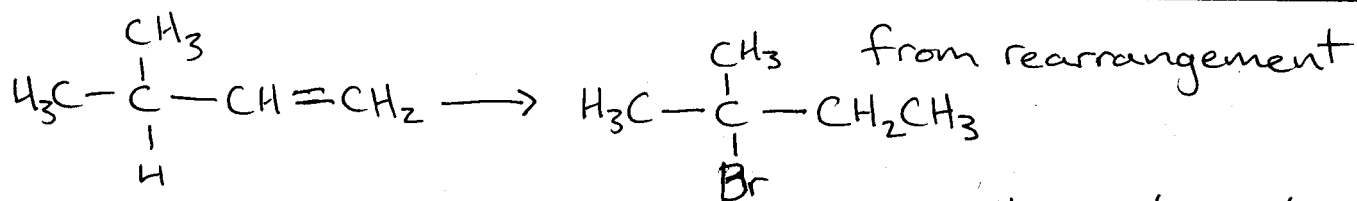
Carbocation Rearrangement

(e.g., in the course of HX addition to alkenes).



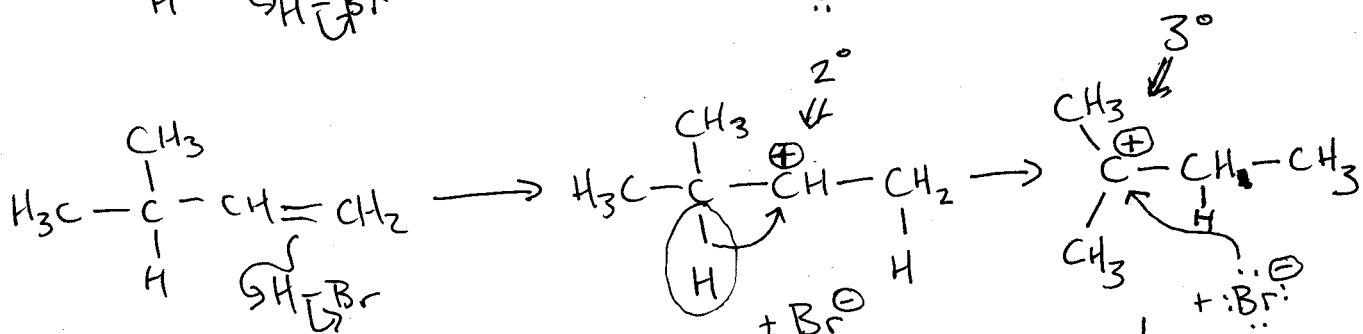
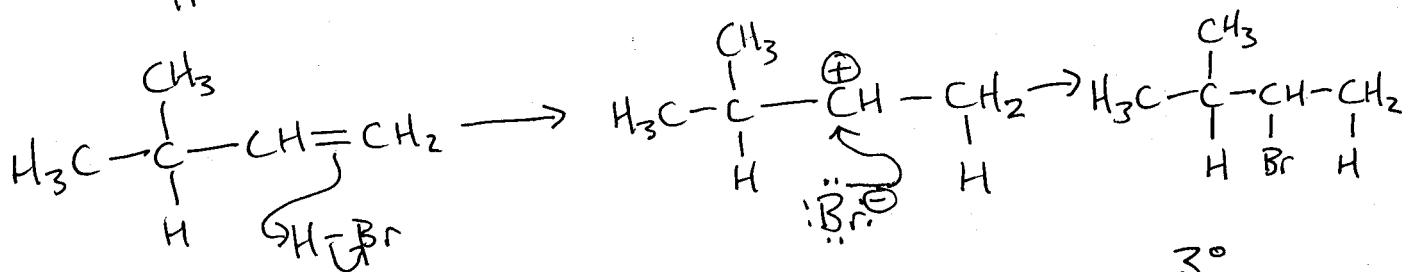
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How do you expand the mechanistic hypothesis to explain this?

Mech. Hypothesis:



Comments:

(1) This process is "1,2 hydride shift"

Proton = H^+
 Hydrogen atom = $\text{H}^\bullet$
 Hydride = H^-

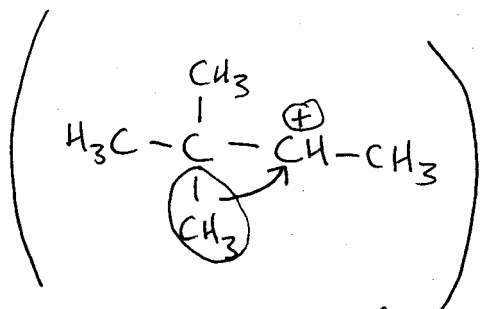
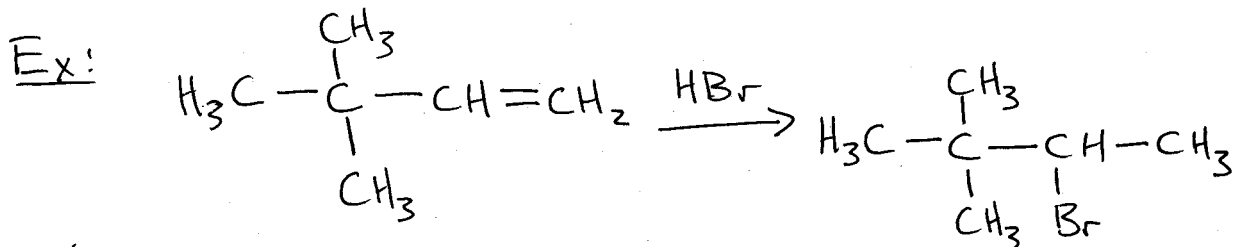
means the carbons involved are ~~not~~ next to each other

3° carbocation was generated.

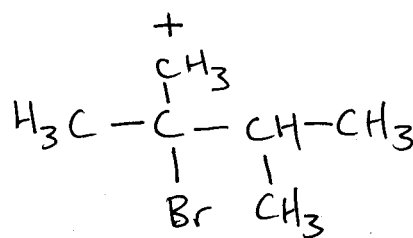
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1,2 alkyl shifts are possible as well



1,2 alkyl shift



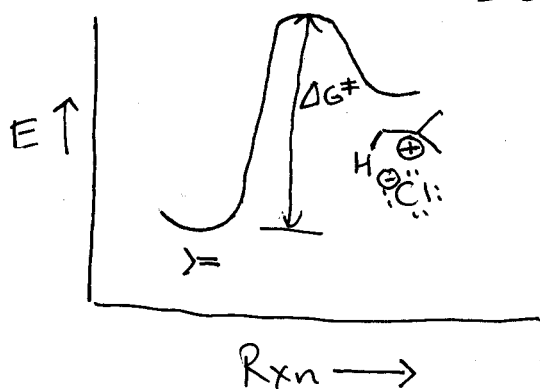
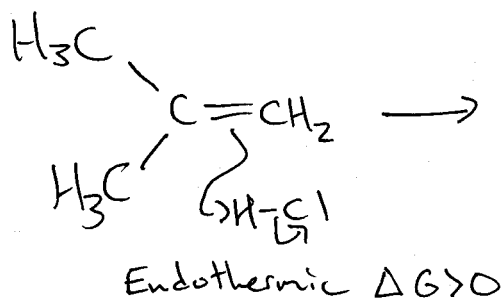
Reaction energy diagrams (Framework for considering Reaction Rates)

⇒ Graphical convention that is complimentary to mechanism/curved arrow convention.

⇒ Energy relationships between or among S.M./Products/intermediates and also between these entities and transition states between them.

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Consider 1st step of an HX add'n



1) carbocation less stable than S.M.

2) Rate determined by $\Delta G^\ddagger$

⇒ Creates great interest in something that cannot be directly known.