

Course 343 Lecturer Gellman
 Day Monday Date 9/28/15
 Notes Taken By Kirandeep Deol Total # of Pages 4

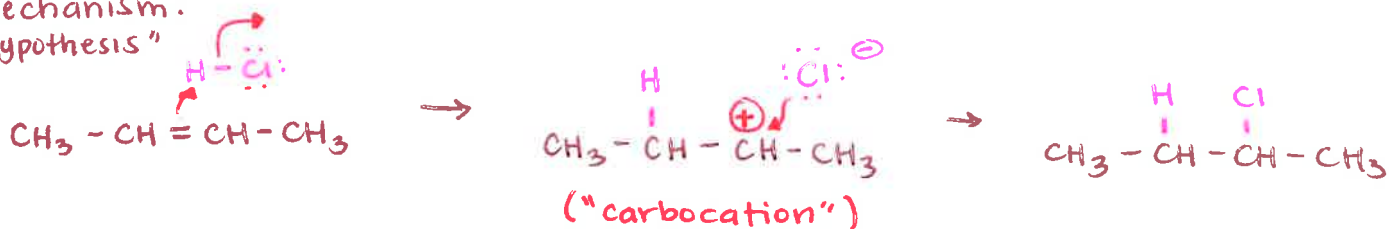
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Recall:

HCl addition to alkenes



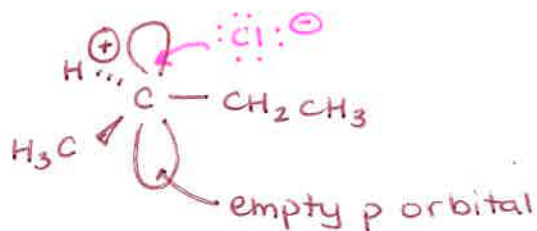
Mechanism:
 "hypothesis"



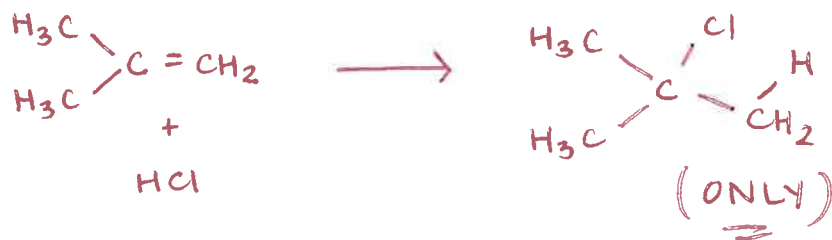
Observe:

1st step - Brønsted acid/base rxn, w/ π e^- as base

2nd step - Lewis acid/base

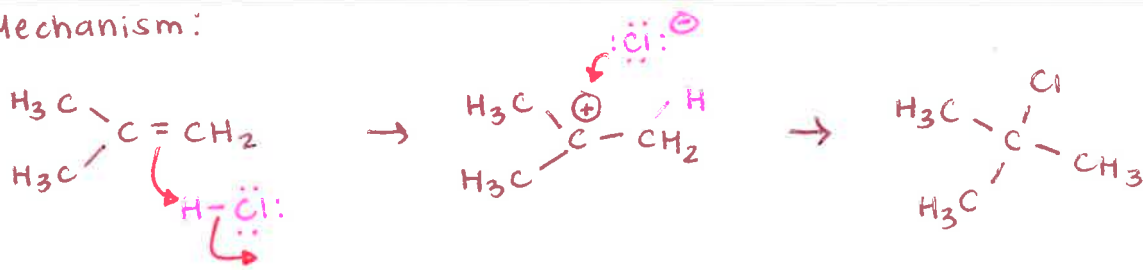


Recall: Unsym. case
 (Markovnikov's rule)

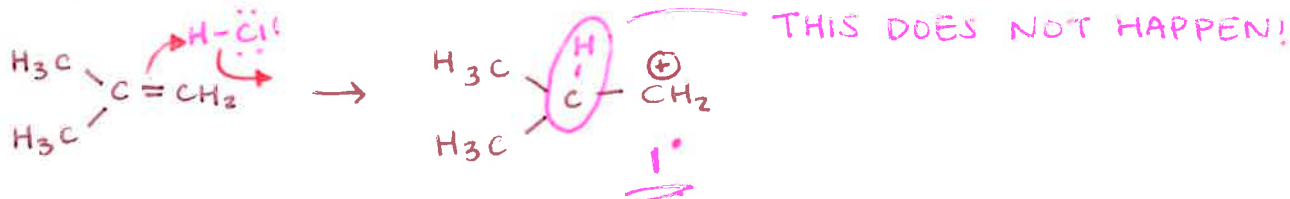


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Mechanism:

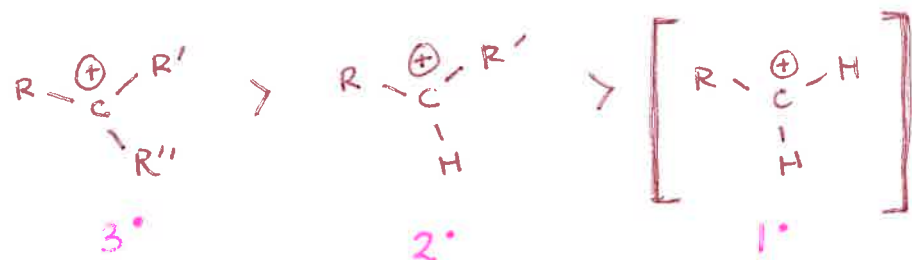


However:



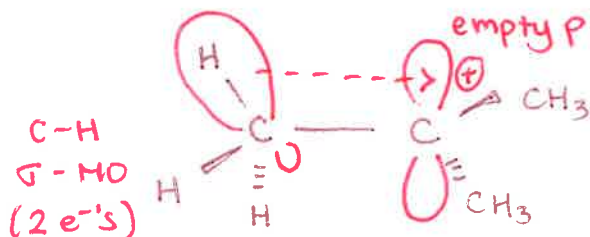
From this sort of trend in HX selectivity (many specific cases), draw conclusions about carbocations....

CARBOCATION STABILITY is strongly affected by # of alkyl substituents



Origin of this trend?

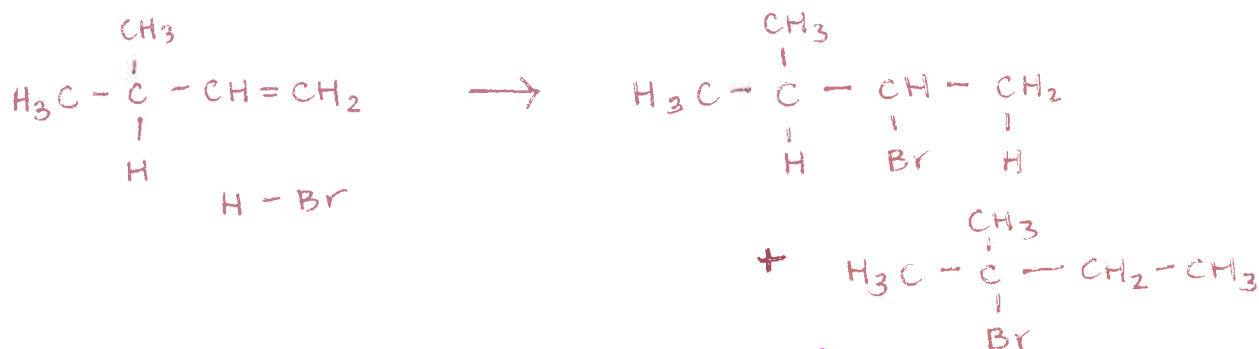
→ Hyperconjugation (e⁻ density shift from C-H σ to empty p)



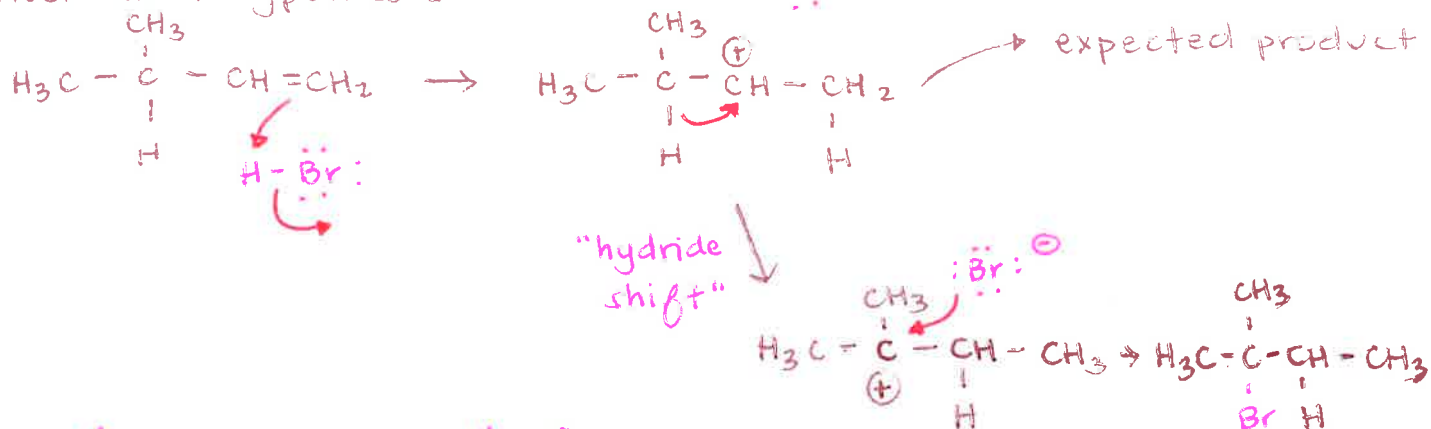
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Carbocation rearrangements - possible in some cases

observe:



Mechanism hypothesis:



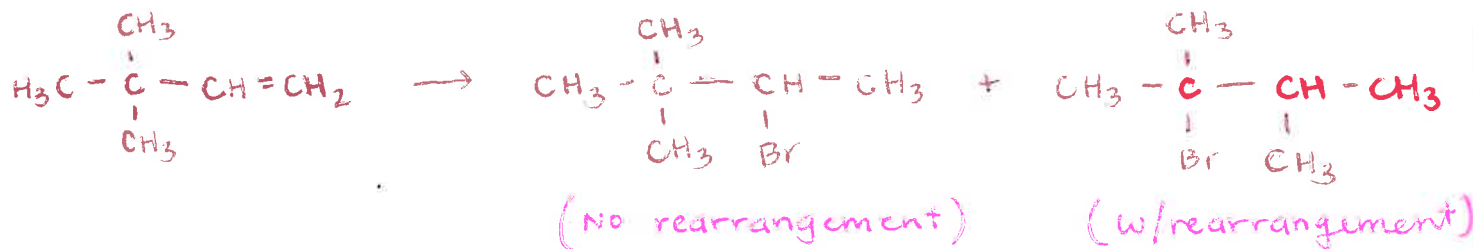
* Note: Hydride is "H:[⊖]"

Why does the rearrangement occur?

carbocation stability! $2^\circ \text{C}^\oplus \rightarrow 3^\circ \text{C}^\oplus$

Alkyl groups can "shift" as well!

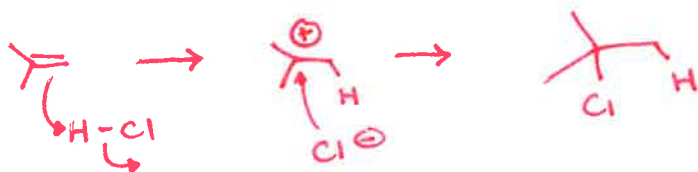
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⇒ You fill in the mechanism.

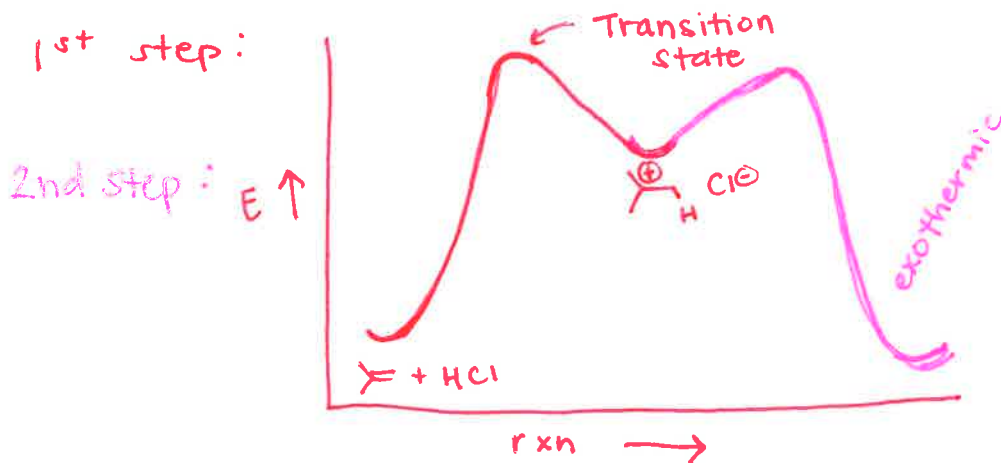
The energetic aspect of rxn mechanisms - reaction energy diagrams.

Recall:



Note: Starting material, intermediate(s), product(s) all correspond to local energy minima.

- There is a local energy maximum (TS) between each pair of adjacent minima.



"rxn →" is some measure of rxn progress

• key point: the carbocation intermediate is a high energy species ("unstable")