Course 343 Lecturer Sam Gellman

Day Wednesday Date 9-28-16

Notes Taken By Nels Gerstner Total # of Pages 4

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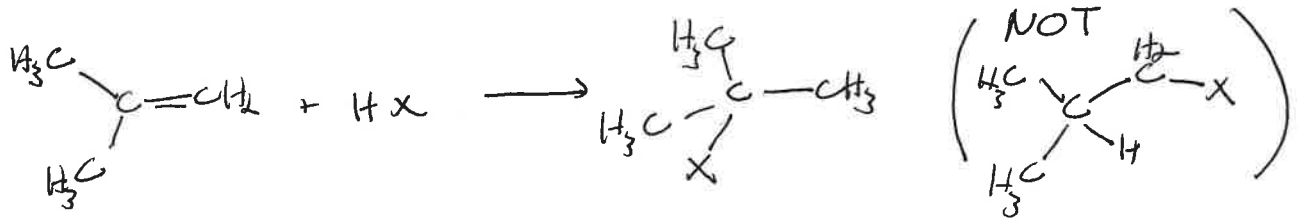
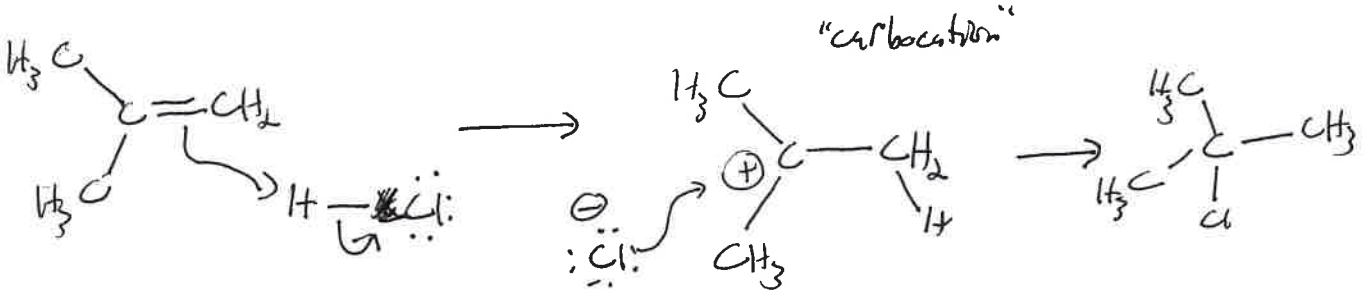
Decall: HX addition to Alkenes

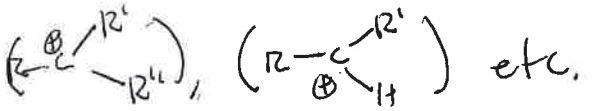


Mechanism

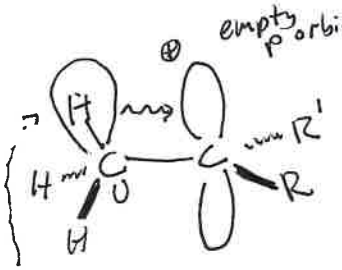


Origin of product selectivity — carbocation stability trend

$3^\circ > 2^\circ > 1^\circ > {}^{\oplus}CH_3$



Why do more alkyl groups around the carbon bearing the positive charge lead to greater carbocation stability? ⇒ Hyperconjugation



The electrons in the C-H bond spend a small amount of their time (a few percent) interacting w/ empty orbital, stabilizing it. This leads to preferential formation of most stable carbocation upon protonation of alkene.

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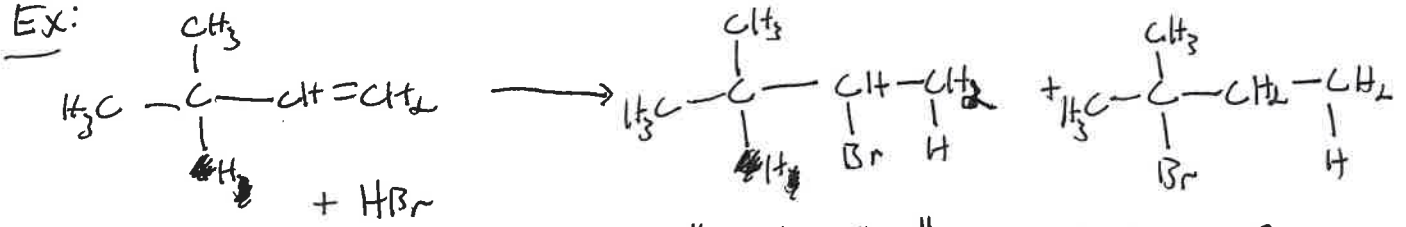
"Carbocation Rearrangements" - sometimes occur in reactions involving carbocation intermediates, such as HX addition.

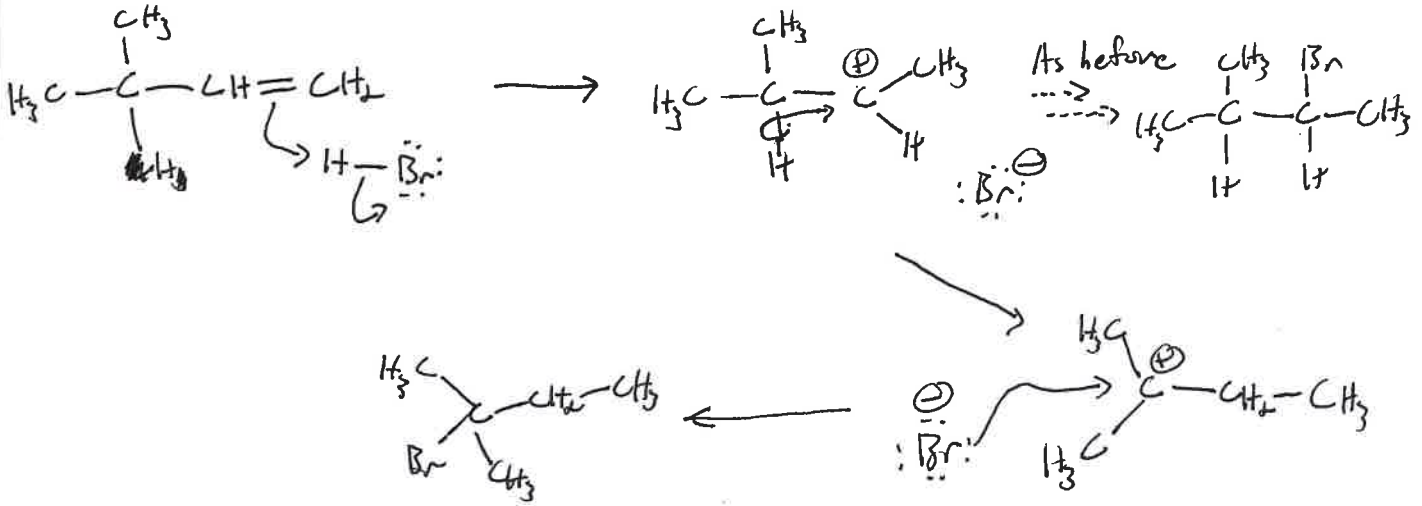
Ex:



"Markovnikov"

Product after $C^{\oplus}$ rearrangement.

Mechanism:



"1,2 hydride shift"

"to the adjacent carbon" → a "$H:^{\ominus}$"

Note: 2° carbocation → 3° carbocation

Driving force for carbocation rearrangements is formation of a more stable carbocation.

Note: Alkyl groups can undergo 1,2 shifts as well.

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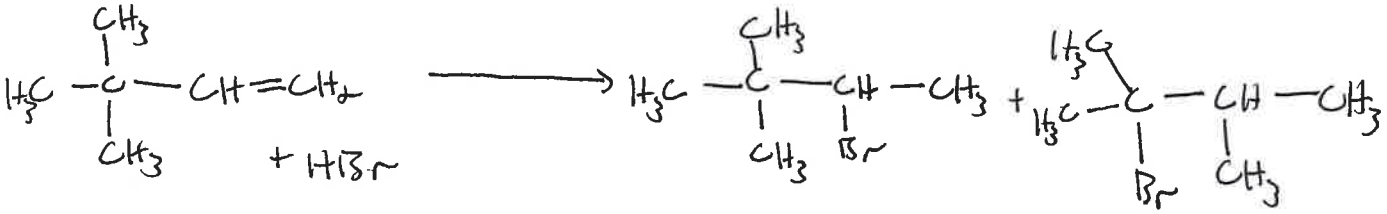
Thus

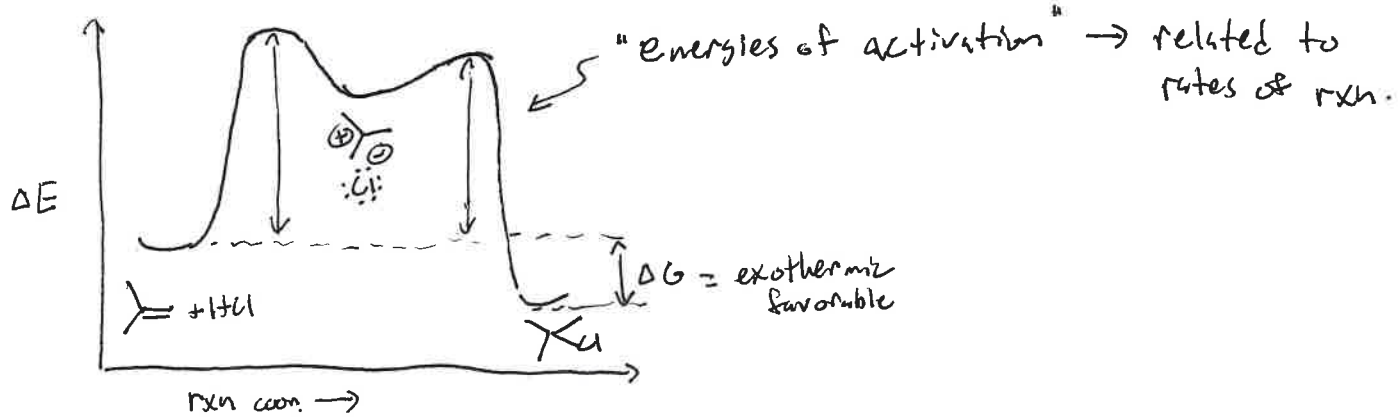


Reaction energy diagrams → complimentary to curved arrow graphics, as they convey ~~relative~~ information of relative energies of starting material, products, intermediates and allows us to predict rates of rxns. Insights in reaction favorability.

∧ maximum → Transition states

∪ minimum → starting material, products intermediates

Recall:



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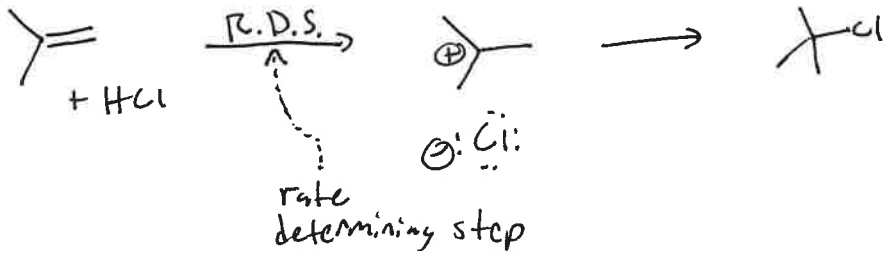
Note: TS #1 ~~[illegible]~~ higher in energy than TS #2. Thus first step in mechanism is rate determining.



Hammond Postulate - Trends in stability of high energy intermediates can be extrapolated to trends in stability of "adjacent" transition states (T.S.).