Course 343 Lecturer Sam Gellman

Day Friday Date 9-30-16

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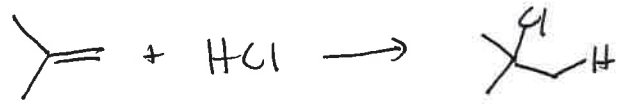
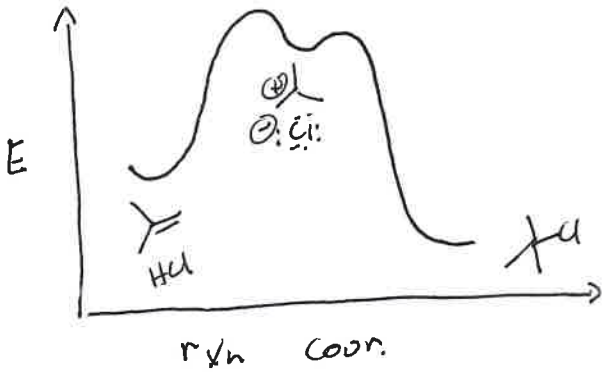
Recall: HX addition...





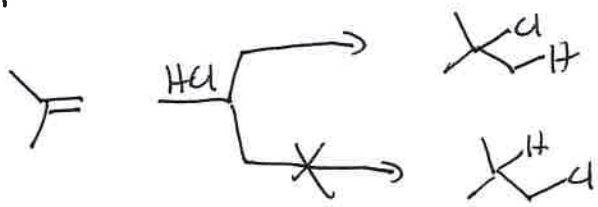
First TS is higher

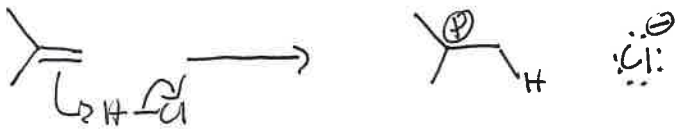
⇒ First step ~~is~~ of mechanism is rate determining for overall reaction.

Hammet Postulate: Structure stability relationship for transition states follow these high energy intermediates (but not for stable molecules such as most starting material and products).

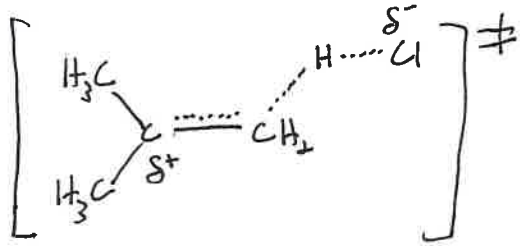
Apply Hammond postulate to HX addition

Rationalize Selectivity (Markovnikov)





consider the TS for this step



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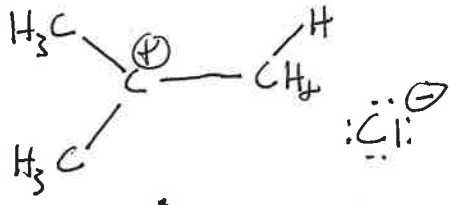
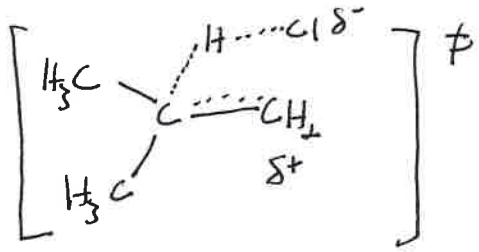


*Intermediate ⇒ Transition state looks like this

Thus, speculate about transition state (TS) that does not occur

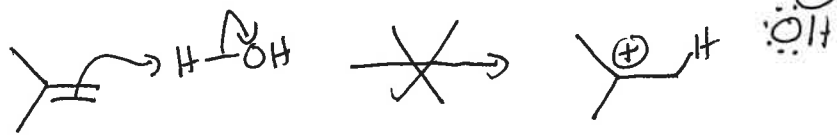


UNREASONABLE

Has primary carbocation like character, which is destabilizing and much higher in energy than putting the partial positive charge on the tertiary carbon.

Variation on the HX additions?

Problem:



Pretty basic, means that H_2O is not very acidic

I.e. H_2O is too weak an acid to transfer a proton to an alkene.

H–OH pka ~16 H–Cl pka ~ –6

Achieve reaction w/ H_2O w/ an acid catalyst.

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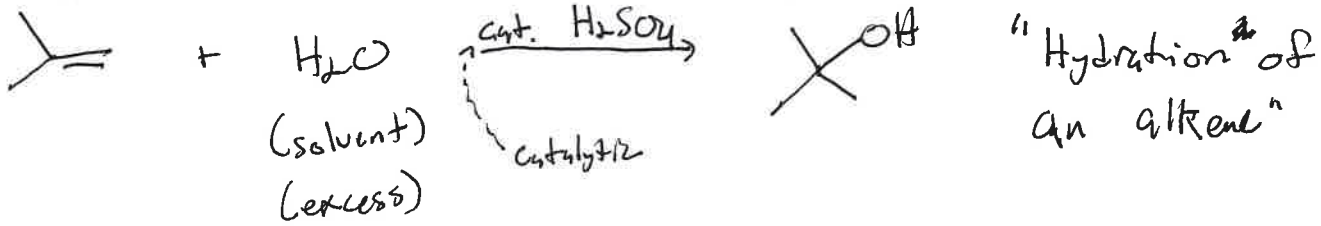
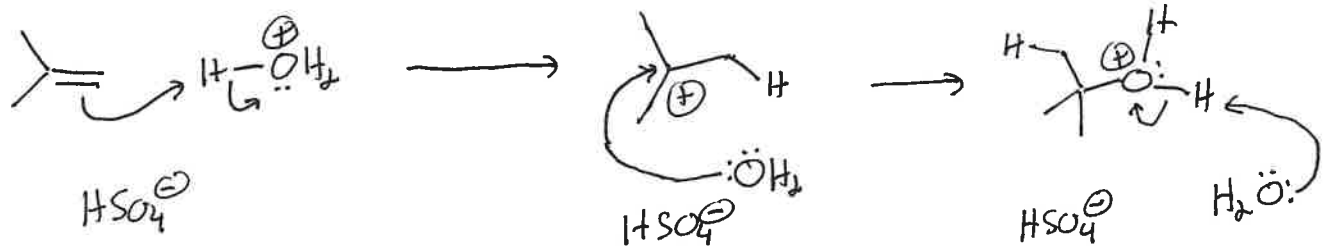
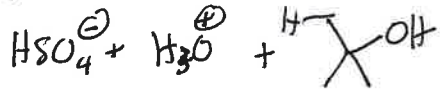


Mechanism:



Note: H_3O^+ regenerated @ end of mechanism ⇒ catalyst

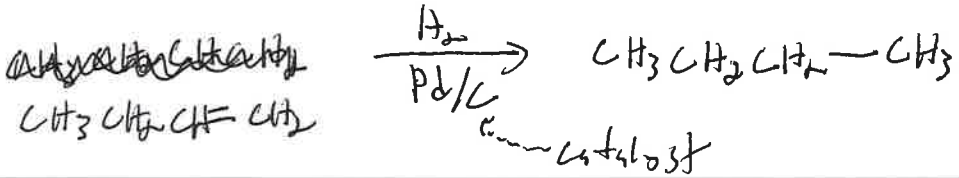


Example of "acid catalysis"

Many manifestations of catalysis in chemistry; phenomenon of high interest, sometimes life consuming.

A different type previously encountered: Hydrogenation of an alkene

Ex:



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Pd/C is the catalyst
("Heterogeneous catalysis")

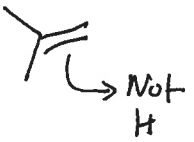
~~Chapter 5~~ Chapter 4 is cut off for the exam next Friday

Chapter 5 – Addition reactions of Alkenes

Rec. problems : 1-22, 27-38, 47-54

So far

Alkene π-system functions as a Brønsted base



π-system functioning as a nucleophile, ie. Lewis Base