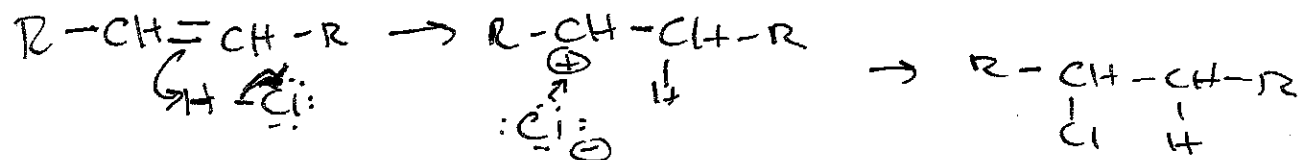


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Recall Mechanism for HX addition to alkenes



Note 1) 2 steps  $\Rightarrow$  "intermediate" (carbo cation)

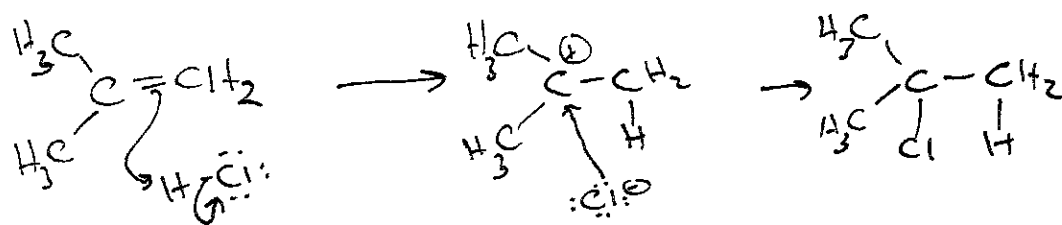
2) Analogies

Step 1  $\sim$  Brønsted acid/base

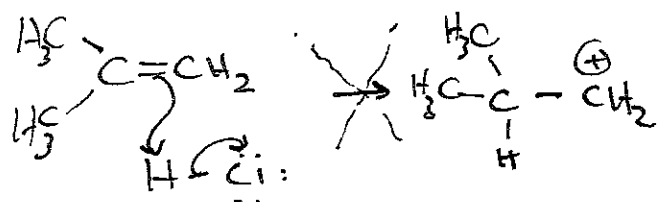
Step 2  $\sim$  Lewis acid-base rxn



Extend mechanistic hypothesis to unsymmetrical alkene

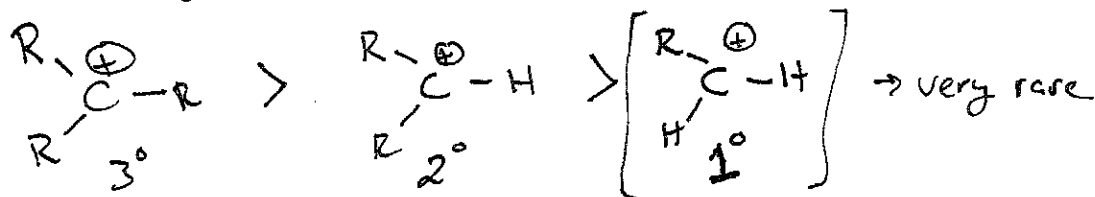


Alternative 1<sup>st</sup> step (that does NOT occur)



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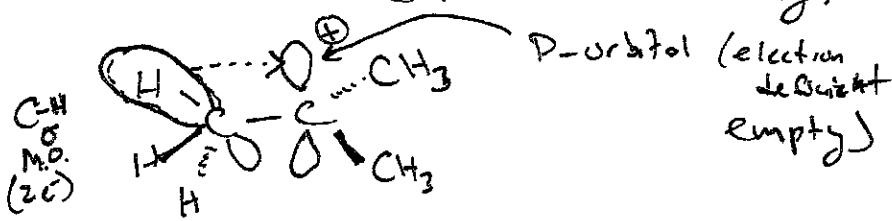
From this and many related observations, conclusions about trends in carbocation stability become evident.



Why do alkyl substituents enhance carbocation stability?

"Hyper conjugation"

Graphically:

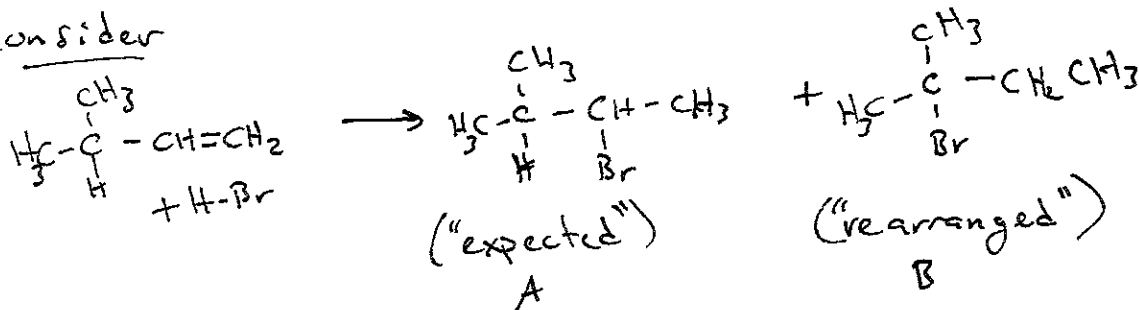


leakage of  $e^-$  from  $CH_3$  to p orbital

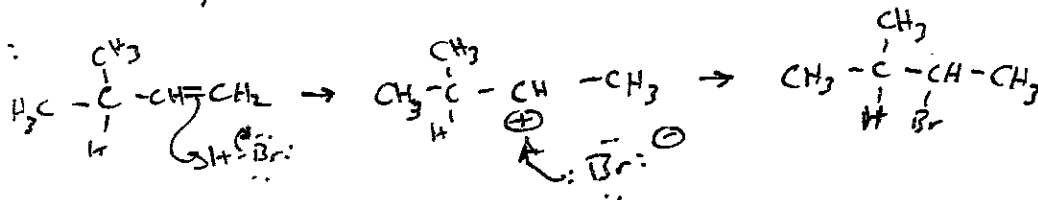
$e^-$  delocalization,  $\sigma \rightarrow p$  delocalization

HX addn w/ carbocation rearrangement:

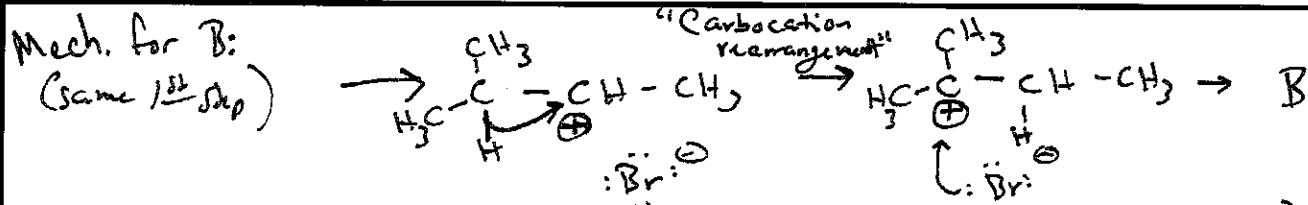
Consider



Mech. for formation of A:



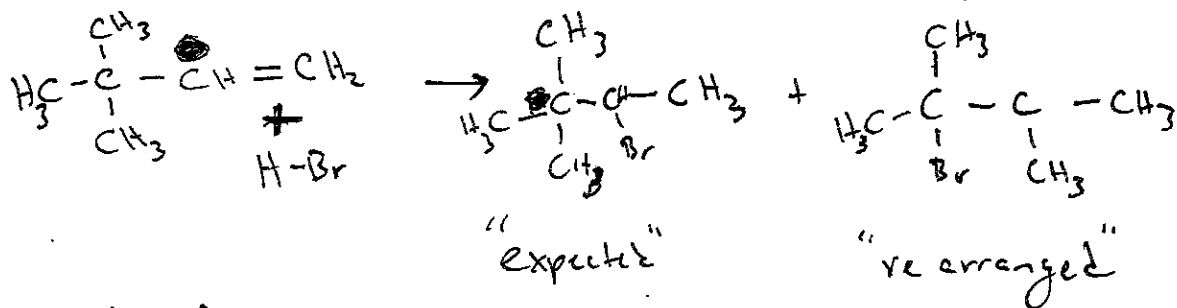
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Carbocation rearrangement  $\Rightarrow$  "Hydride shift" ( $\text{H}^-$ )

Driving force for carbocation rearrangement = increased stability  
 ( $2^\circ \rightarrow 3^\circ$ )

Alkyl groups can shift in  $\text{C}^+$  rearrangements



You fill in mechanism

A second graphical formalism for conveying info about rxn mechanisms  $\rightarrow$  Energy Diagrams

Mechanisms  $\rightarrow$  Energy Diagrams

- relative energies  $\left\{ \begin{array}{l} \text{S.A. vs. intermediates vs. products} \\ \text{(local energy min)} \end{array} \right\}$

- relative energies of transition state (local max)