Chem. 131(231)A; prob set 3

1. Consider the reaction of 2-methylpropene (isobutylene) with HCl.

- Two products can form.
  What are they?
- One of the products dominates.
  Which one?
  Why?
- Formulate a mechanism illustrating the formation of each of the products.
- Draw a potential energy diagram to illustrate the overall sequence.
  Which step is rate determining?
  Will the transition state for that step occur 'early' or 'late'?
- Draw a picture of the transition state leading to the major product.
- Which product should be formed faster?
  What is the basis for your response?

{**Notice** the utility of the Bell-Evans-Polanyi and Hammond postulates in formulating your responses.}

2. Determine ΔH for the reaction of ethylene with H-Br to form bromoethane.

3. Predict the reaction that you'd expect to display the greater temperature dependence. Provide a rationale.

A + B reacts to afford C + D
or
A undergoes fragmentation to produce C + D + E

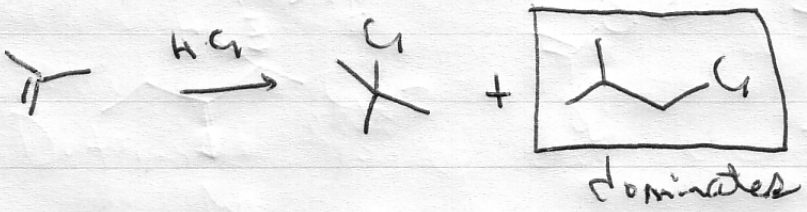
4. Illustrate the Claisen condensation of ethyl acetate using sodium ethoxide as the base.
   Why would one be ill-advised to use sodium methoxide, instead?

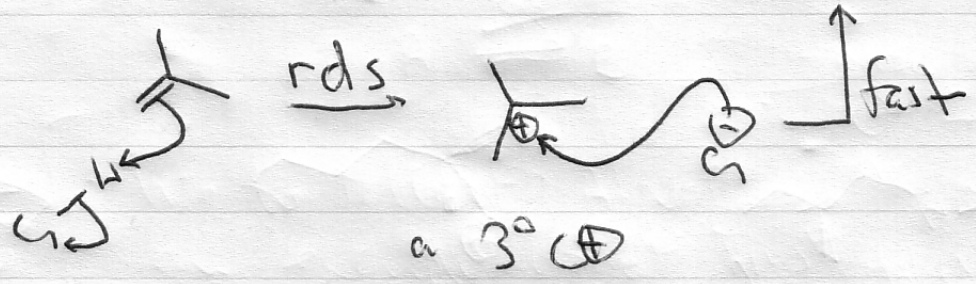
5. Formulate a mechanism to illustrate that a heteroatom-stabilized carbocation is an intermediate in:
   [a] the acid catalyzed formation of a ketal
   [b] acid catalyzed deketalization
   [c] the formation of an imine (Schiff base)

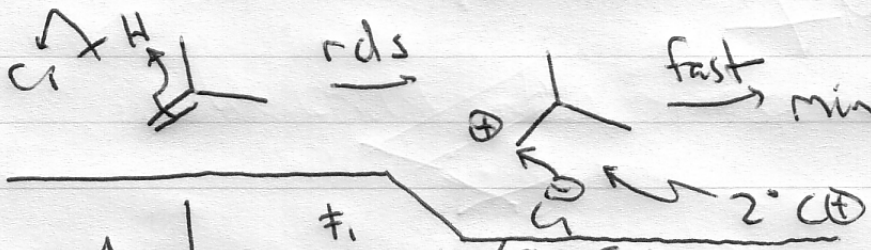
Draw a molecular orbital array to illustrate how the heteroatom is able to stabilize the cation. Notice how your response incorporates both stereochemistry and electronic effects/influences. This is an example, therefore, of a ***stereoelectronic*** effect.

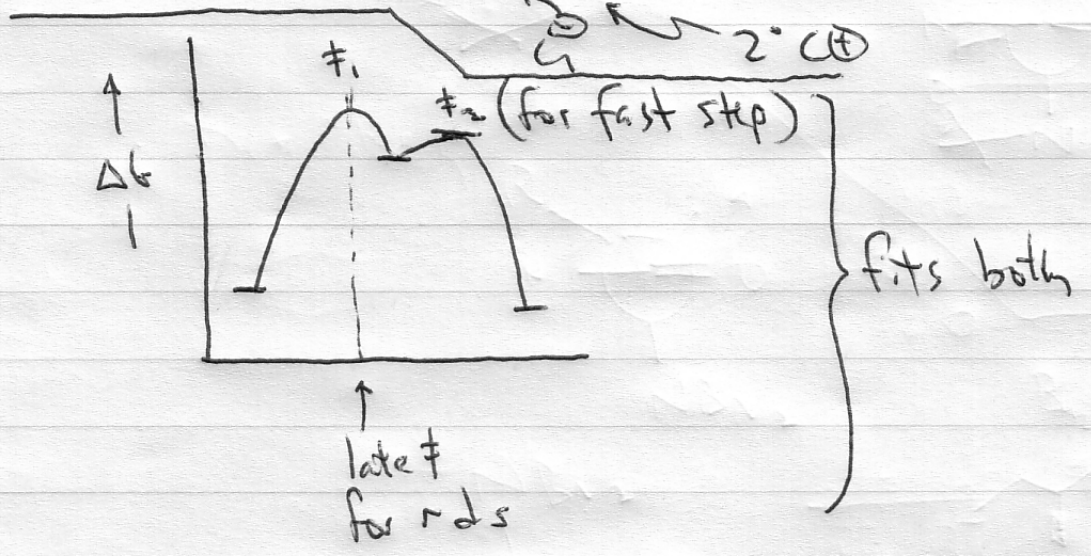
Solns, Set 3; Chem 131(231)A

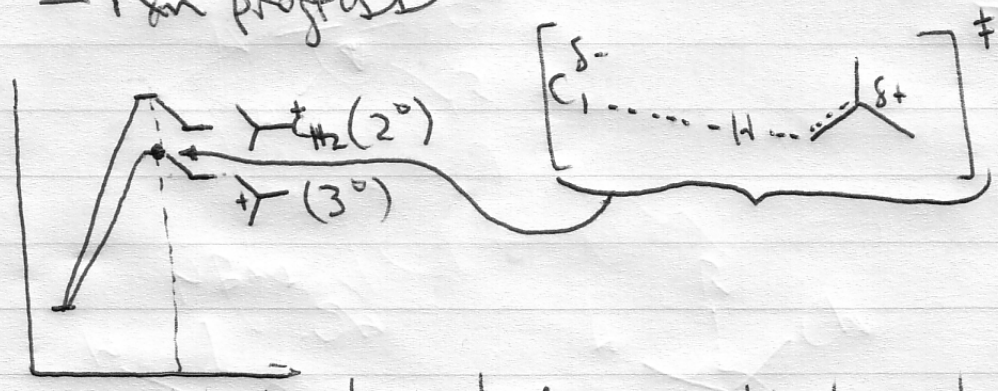
1.





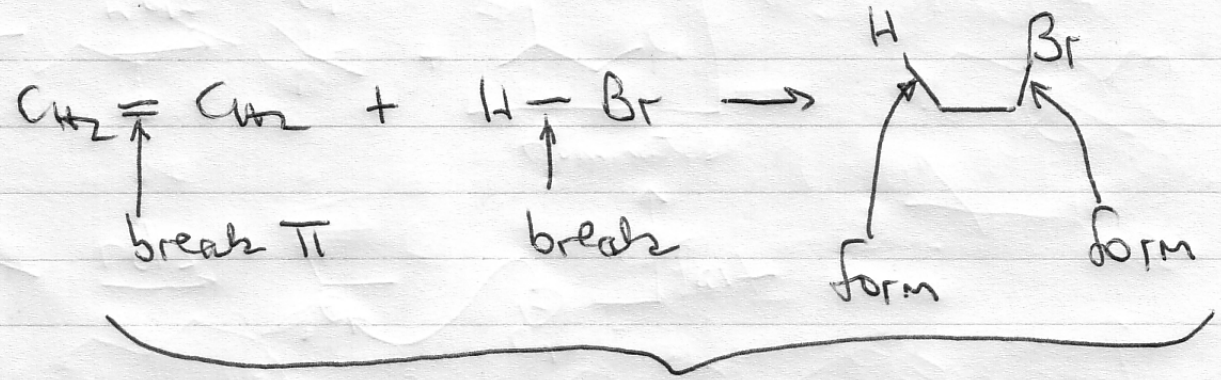






late ‡'s that look more like the intermediates than the starting materials. 3° ⊕ is more stable than 2° ⊕ $\Rightarrow E[\ddagger(\to 3°)] < E[\ddagger(\to 2° \oplus)]$
$\Rightarrow$ rate for $\{ \text{alkene} \to \text{X-C} \}$ > alternative

2.



Look up these numbers & calculate ΔH using them.

3. $A + B \rightarrow C + D$ – no entropy change overall.

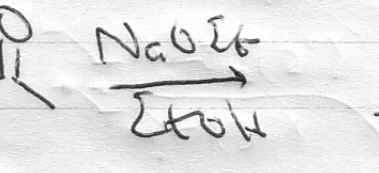
vs

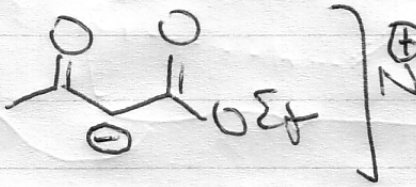
$A \rightarrow C + D + E$, a process wherein ∃ a significant increase in ~~ext~~ entropy.

This ⇒ there should be a considerable contribution from $T\Delta S$ in ΔG since

$\Delta G = \Delta H - T\Delta S$

So, this process should display a > T-dependence.

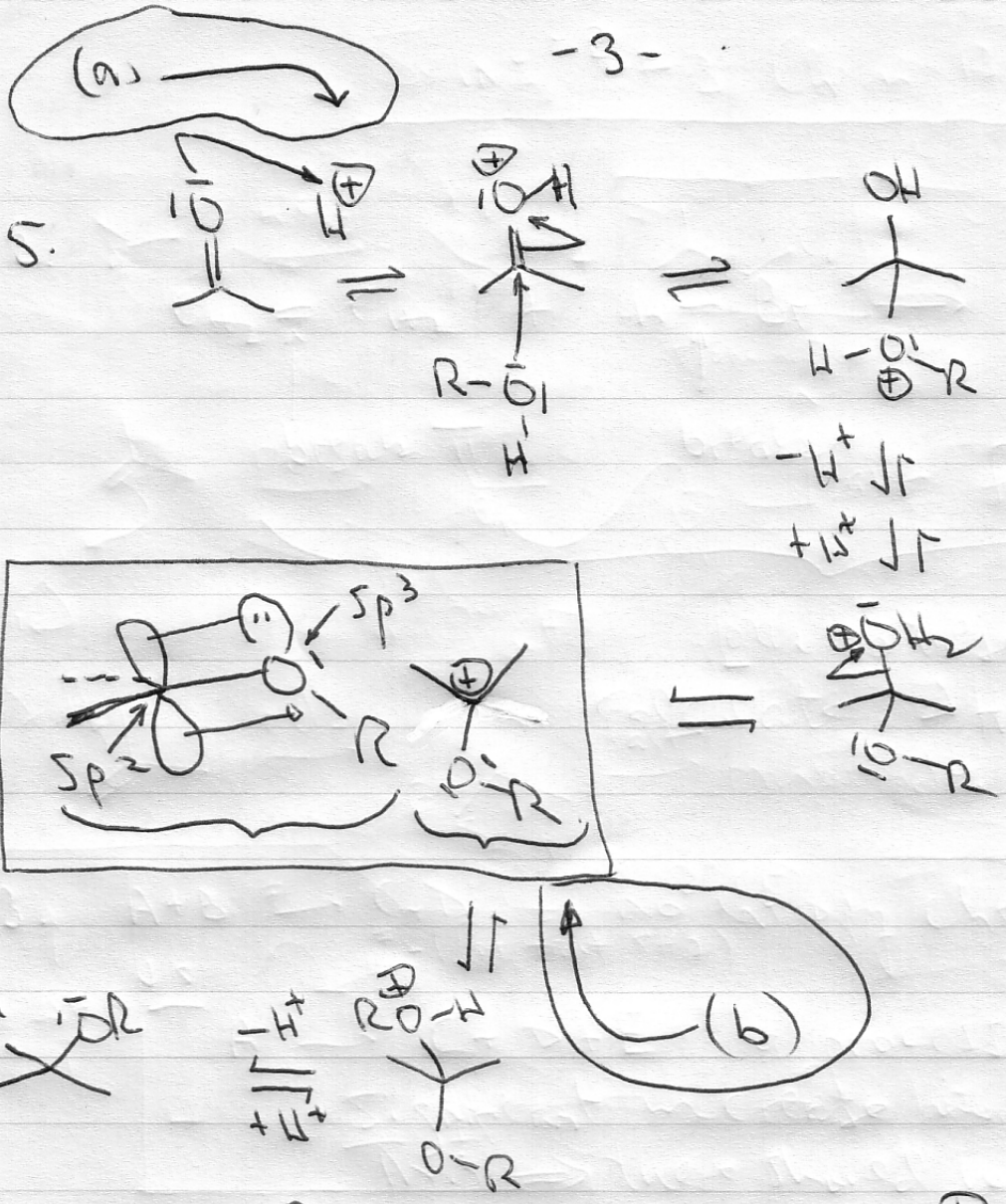
4. 2 EtO– 



if OMe then can have as side reactions, the following transesterifications

and w/ the product β-keto ester, too.

5.



(c)