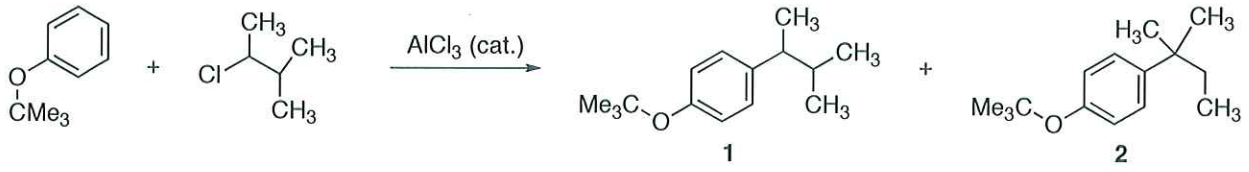
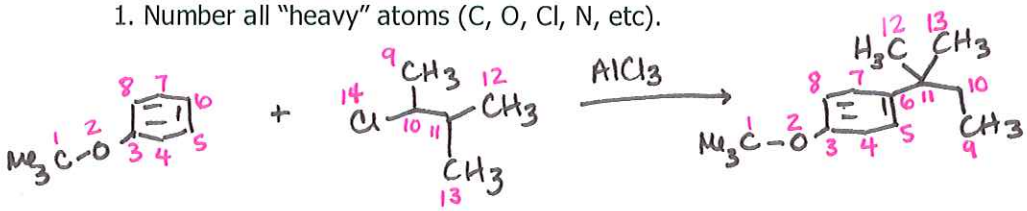
Prof M's Strategy for Solving Mechanism Problems

Here are the steps I use to figure out a reasonable mechanism for a new reaction. I will work through the following example to show how each step is applied.

Ex: In addition to expected product **1**, product **2** is formed under the following reaction conditions. Please draw a reasonable arrow-pushing mechanism that illustrates how product **2** is formed.

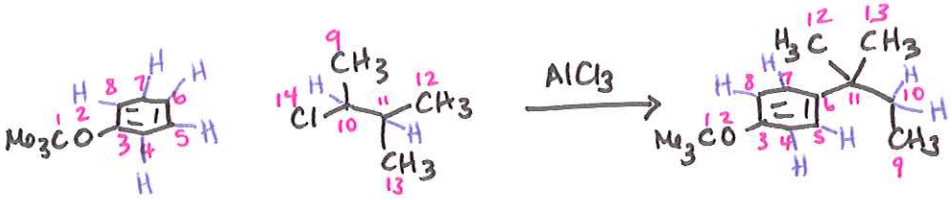


1. Number all "heavy" atoms (C, O, Cl, N, etc).



Try to map atoms of starting material onto product. If you're not sure, put a * next to that #. (You can always revise your numbering if your initial #'s are wrong.)

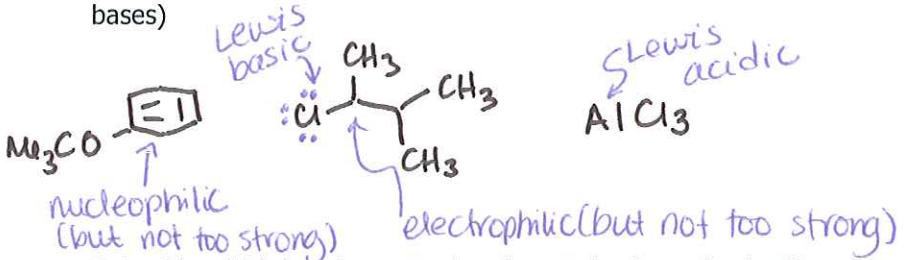
2. Draw in hydrogens.



3. Inventory the bonds you need to break and the bonds you need to make.

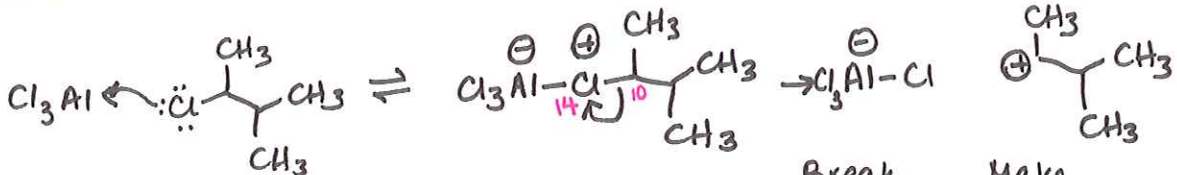
Break	Make
C6-H	C6-C11
C11-H	C10-H
C10-C14	

4. Consider the starting materials. What is nucleophilic? What is electrophilic? (or identify acids and bases)



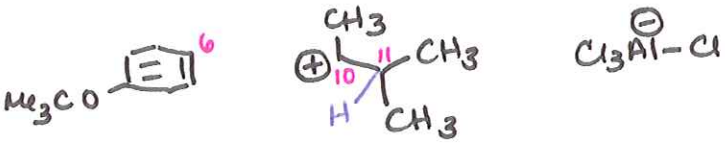
5. Decide which bond you can break or make first. Check off your break/make table from step 3.

Lewis base + Lewis acid...



Break	Make
C6-H	C6-C11
C11-H	C10-H
✓C10-C14	

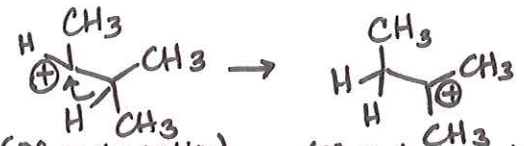
6. Repeat steps 4 and 5 until you get to product. If you come to a step where there are 2 possibilities about what do to, choose one and put a star next to that step. If you cannot then get to the product, return to that step and see where the other possibility takes you.



nucleophile — hot electrophile

Combining these: Make C6–C10. Bad! C6–C10 is not in our table (step 3). Choose a different option from Break/Make Table.

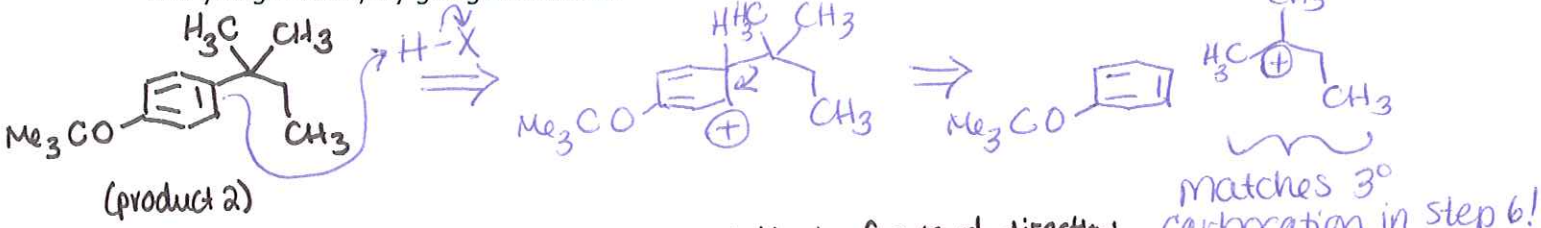
Break	Make
C6–H	C6–C11
C11–H	C10–H → 1,2-hydride transfer!
✓C10–C14	



(2° carbocation) → (3° carbocation)

Broke	Made
C6–H	C6–C11
✓C11–H	✓C10–H
✓C10–C14	

7. If you get stuck, try going backwards.

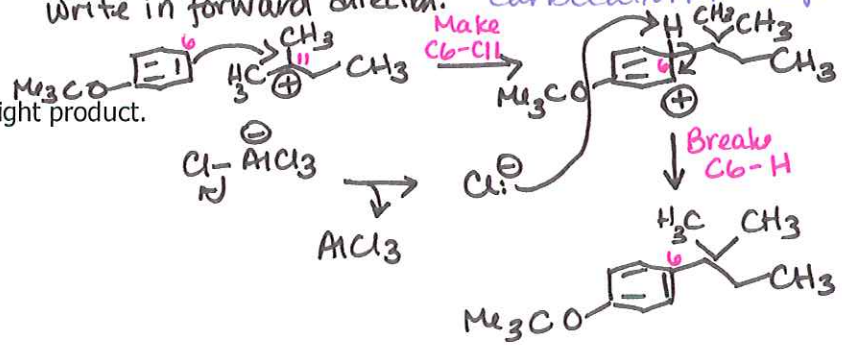


(product 2)

Looks like an electrophilic aromatic substitution, so last step is always deprotonation...

matches 3° carbocation in step 6!

Write in forward direction:



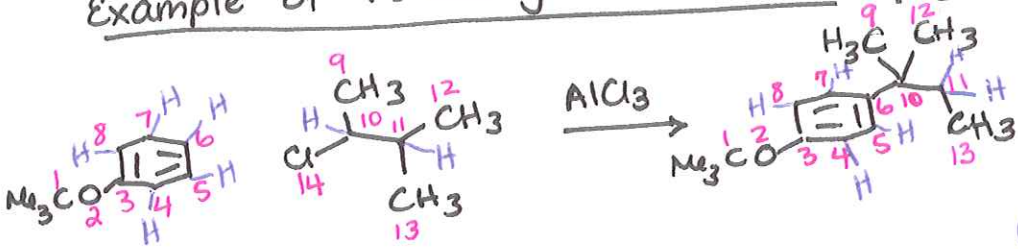
Make C6–C11

Break C6–H

8. Confirm that the product you form is the right product.

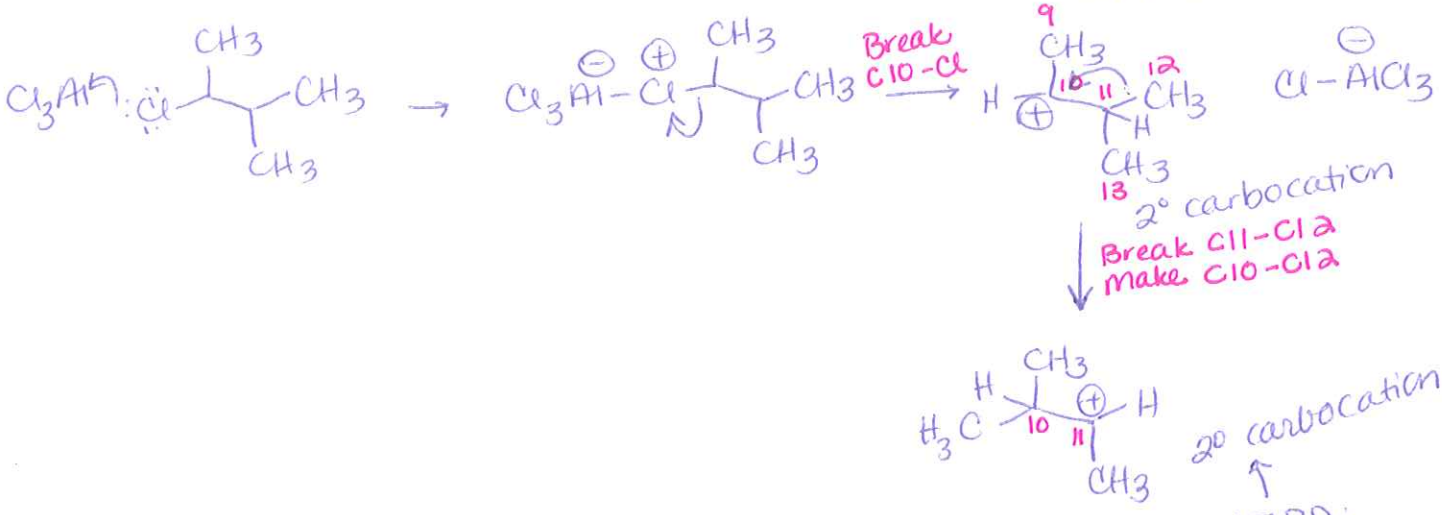
It matches 2!

Example of Following the Wrong Path (at first):



Break	Make
C6–H	C6–C10
C10–H	✓C10–C12
✓C10–Cl	C11–H
✓C11–C12	

(seems like a lot of Hydride & Alkyl Shifts)



↑ WEIRD; carbocation rearrangements usually occur if more stable carbocation can be formed. Not the case here.

Also → the 2 carbocations are THE SAME!!

This is where I would re-evaluate the choices I made.
It seems like I'm doing a lot of extra bond breaking & making.
1st choice I made: Numbering atoms in my product. Maybe the carbon that ends up on C6 is not C10, but rather C11. Start over w/ new numbering & see if you get a more reasonable mechanism.