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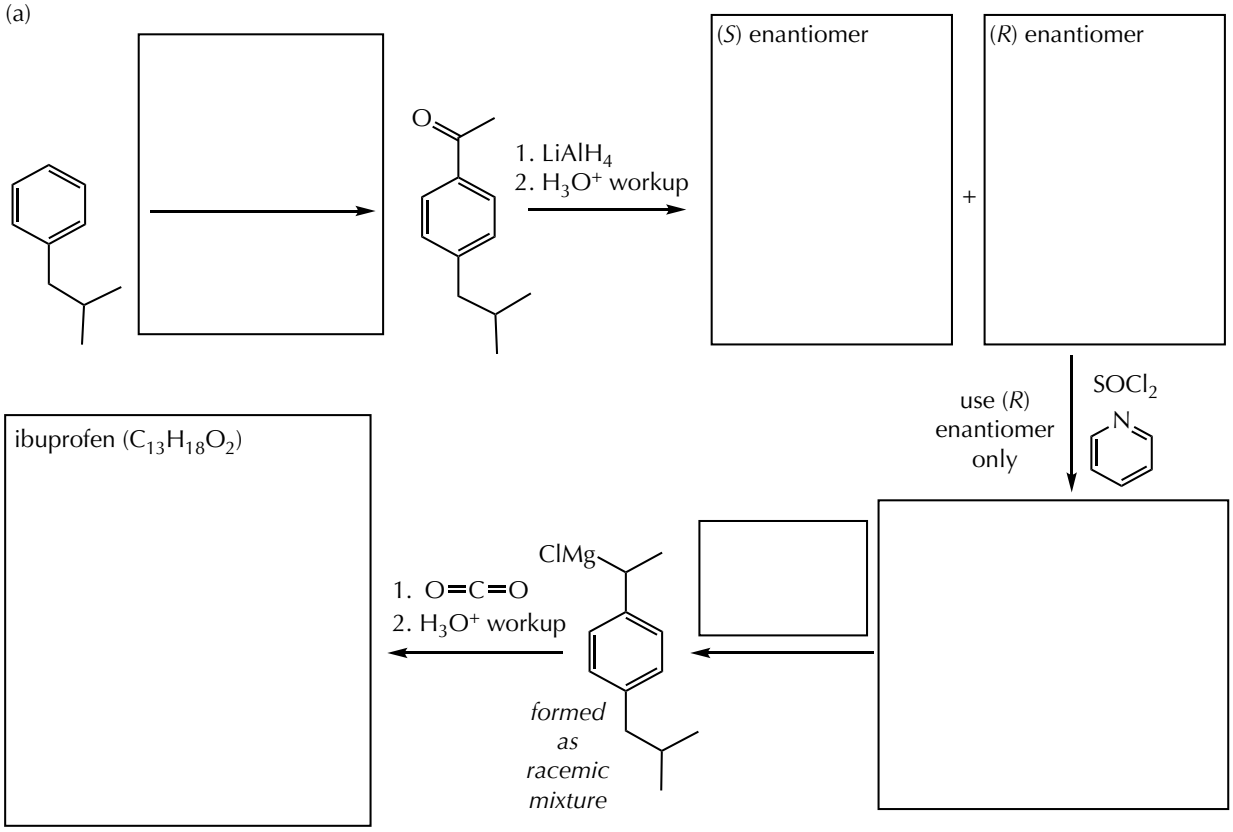
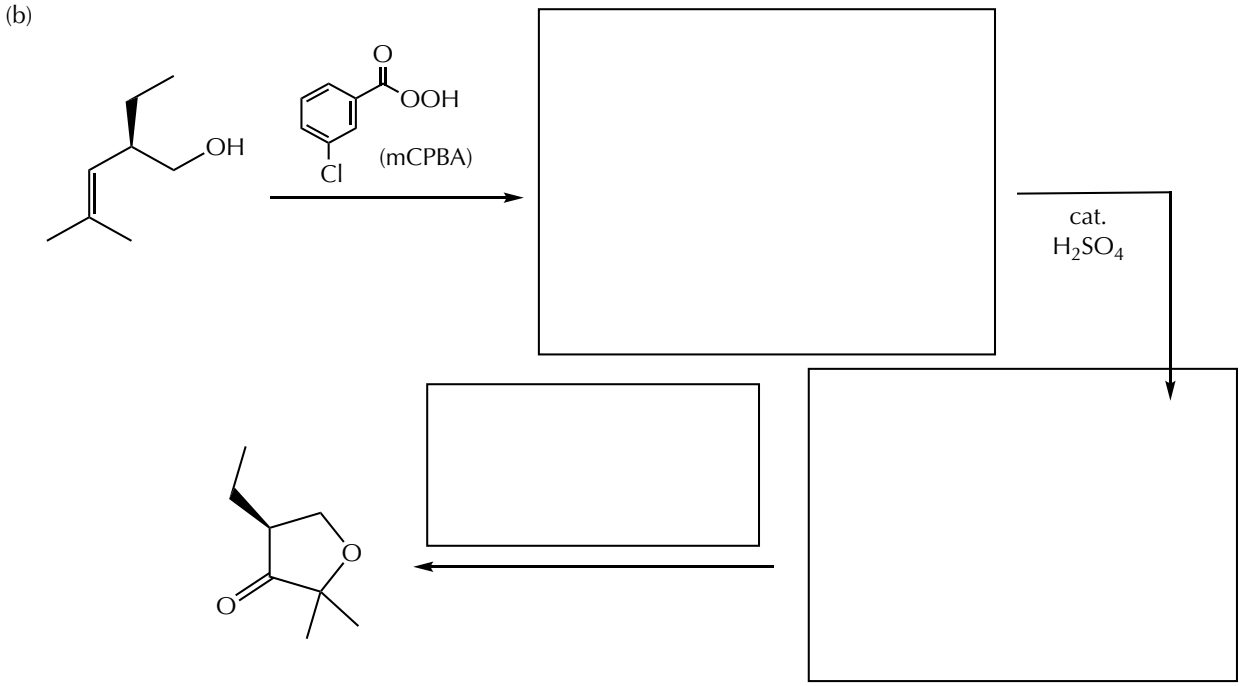


(b)



Chemistry 215 • Thinking in Blue • Week 03

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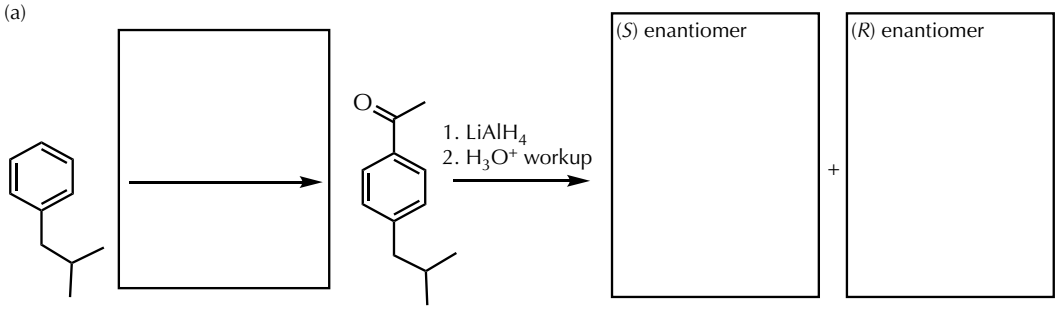
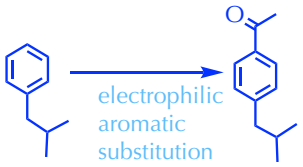


All kinds of questions, and particularly transformations, rely strongly on a deliberate classification or identification step, so that you can make one relatively easy, non-detailed decision, that tells you what area you are working in. This step is often under-appreciated in its value. Take a look at the first step:

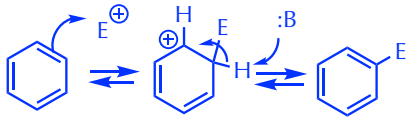


Imagine, for instance, that the text of the problem actually included "electrophilic aromatic substitution" under the arrow. By including this phrase, two things are simultaneously true: (a) the question is easier to answer, and (b) the decision still tells you nothing about what details are needed, but you know what to think about. Therefore: identification is an important skill to learn, in and of itself.

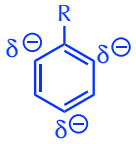
So: it is critical to be able to correctly identify ("diagnose") a question, to be able to draw from the proper information to solve it ("treatment"). The diagnosis alone does not provide the details you need, but for sure: if you get the diagnosis incorrect, it does not matter what you write after that because the correct "treatment" for the incorrect "diagnosis" is simply the wrong answer — although it will feel as though you are working correctly because, in one sense, you are; but you would be answering the wrong question.

The details of Electrophilic Aromatic Substitution cannot be figured out from this information. You either understand it or you do not. Recall that, in general, strong electrophiles (E^+) undergo the addition-elimination reaction known as EAS.

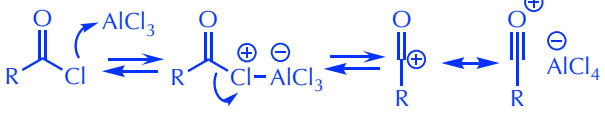
general mechanism

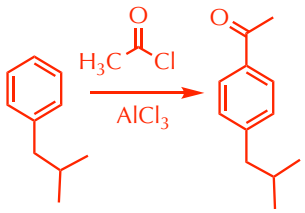


regio-directing effect of e-donor groups (p>o)

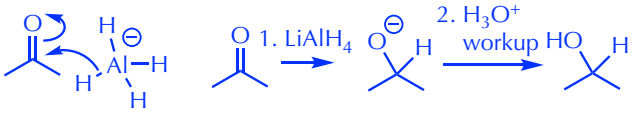


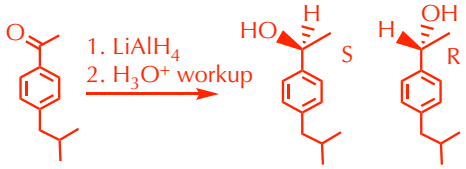
conditions for forming carbonyl-based E^+





The lithium aluminum hydride ($LiAlH_4$) reaction provides a strong nucleophilic source of hydride that, among a few other reactions, commonly participates in carbonyl addition reactions. There needs to be a second, separate protonation step to form the OH bond from the intermediate oxygen anion. The fact that there are two enantiomers formed is a reminder about where the reaction takes place, as the text is saying there is a new stereocenter forming.





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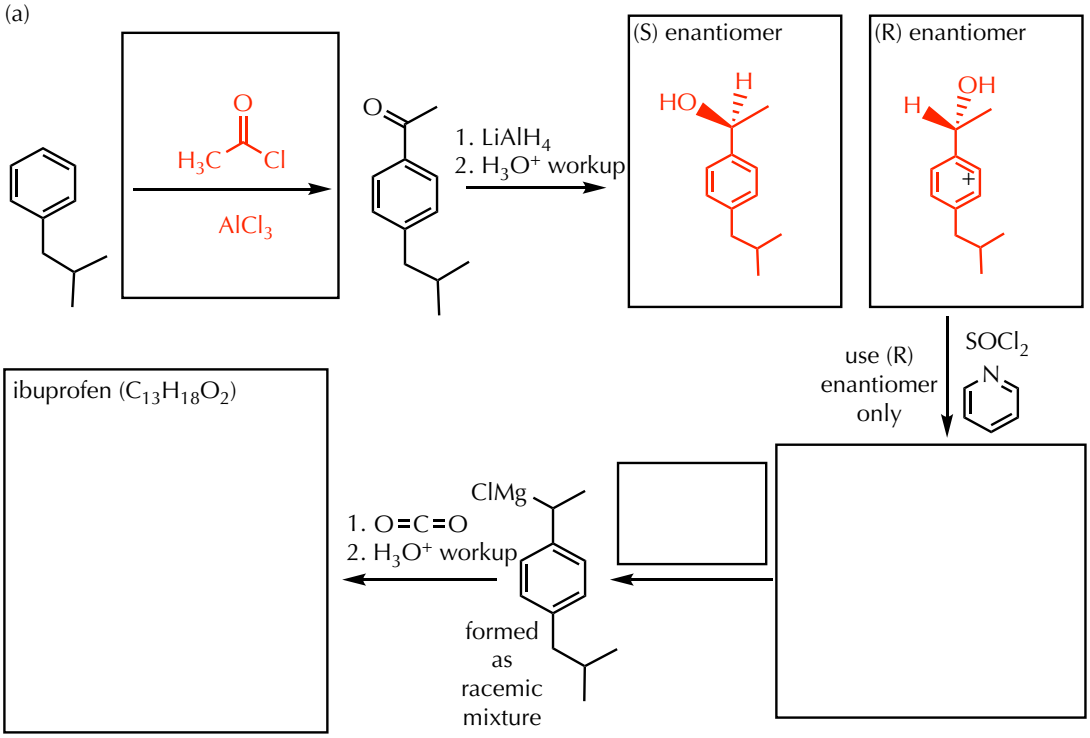
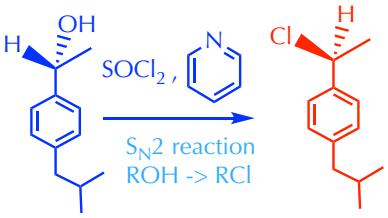
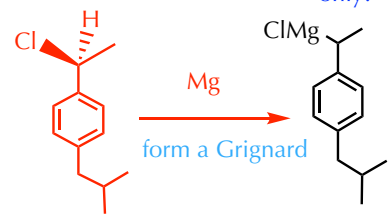
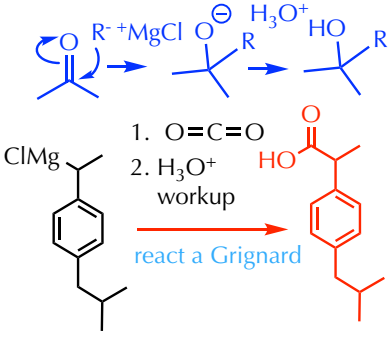


Continuing on, the story is the same. You cannot "figure out" what $SOCl_2$ and pyridine do by inspection of the reagents. These are transformation reagents associated with a particular concept, namely, "S_N2 reaction of alcohols to chlorides" (a direct comparison to the PBr_3 reagent from an earlier "Problem of the Week"). Starting with the "R" enantiomer of the alcohol, it means a substitution resulting in inversion of configuration (and not other stereoisomer). Notice once again how the general identification of the reaction is key to answering the question.



In the next step, you need to see the distinctive feature of the organometallic compound, a Grignard Reagent. As it is here, it might be represented in a covalent form, or it might have been represented in an ionic form $R^{-}\ ^{+}MgCl$. Notice also the clue about the prior part: this structure has a chlorine in it, so if you forgot what $SOCl_2$ did, there is a chance of remembering, here. Again, the answer to the question "how do you form a Grignard Reagent" is not deducable, only the identification is possible from the given information. You need to then provide the rest: R-X + Mg^0 -> R-MgX (breaking the R-X bond means losing the stereochemical configuration, so it says "racemic"). Finally, the question becomes "how does a Grignard Reagent react?" And typically, it adds to C=O groups (much as the $LiAlH_4$, earlier; see right), followed by protonation of the alkoxide intermediate (as earlier). Molecular formulas are great information. The Grignard is $C_{12}H_{17}ClMg$, which means that the elements from CO_2 and one H are needed.





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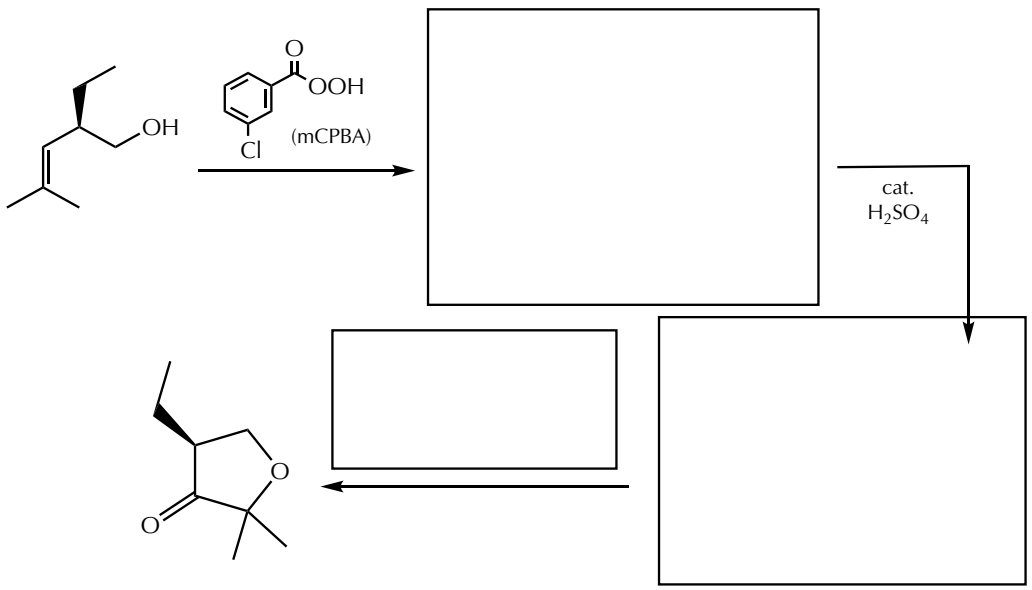
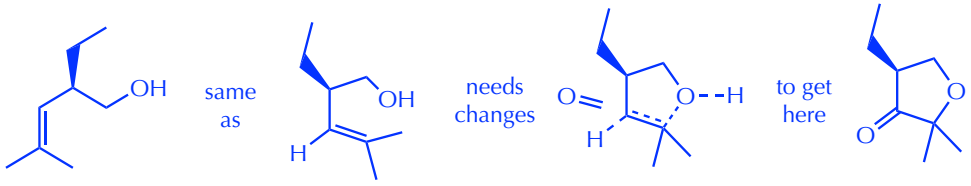
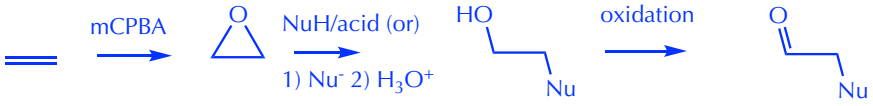


This multi-step transformation question can be solved step by step, but in fact it is much easier when all of the information is used at once. The key relationship is between the starting material and the final product. If you can deduce the general relationships and think about what is gained and what is lost, and how, you can figure out the entire solution (in general) and then just fill in the specifics. That is: first, it is important to note that all the carbons are present, still in the product, and there has been one oxygen atom added and two hydrogens have been lost.



The bonding changes that take place are all around the double bond, and the mCPBA reaction (alkene to epoxide) is important because that introduces an oxygen atom AND because the follow-up chemistry of epoxides is that they can open under acidic or basic conditions. Opening the epoxide leaves an alcohol, and that is needed to make a C=O via oxidation chemistry. Always stick with the known chemistry!



If you sketch out this general solution, you can see if it makes any sense. Then, when it does, you have the confidence to go in and fill out the details. Conceptualize the solution before writing stuff down.