The What, How and Why of Problem Solving in Organic Chemistry… and elsewhere!

> The Master said, "Learning without thought is labor lost; thought without learning is perilous."
> The Master said, "To attack a task from the wrong end can do nothing but harm."
> The Analects of Confucius (K'ung Fu-tsu, ca. 500 BCE), 2-15 and 2-16.

Preamble

It is an unfortunate fact that few high-school graduates today are given the serious intellectual challenges that require them to develop problem-solving skills. It is even more unfortunate that the more talented the student, the less likely it is that he or she has ever been pushed to the limits of what can be achieved by simple "inspection". In consequence, many students arrive at university to find that they are ill equipped to deal with more complex problems that do not yield up their secrets to the first glance.

Problem solving is a process of exploration. Like historical explorers, students embarking on a problem need to equip themselves with as much *knowledge* as possible about the territory to be explored. Most university students are reasonably good at acquiring knowledge, if by "knowledge" one means "a compendium of facts". However, most students have given little thought to organizing their factual knowledge in such a way that it is accessible in a context other than the one in which it was first learned.

Both the explorer and the student also need *techniques* – navigation, surveying, mapmaking, organization, and discipline among other things – if they are to succeed. Knowledge is useless without technique, and technique is useless without knowledge. As Confucius pointed out 2500 years ago, you cannot expect to succeed by simply memorizing facts without context or concept, nor is it wise to concentrate on the "general ideas" without a solid grounding in fact.

Drawing on the metaphor of exploration, I will show you a technique for approaching complex problems, and how this technique should influence the way you learn new factual material. While my focus will be on problems in introductory organic chemistry, I think this approach is relevant to any situation in which you need to absorb a new situation, figure out what is going on, and what you are going to do about it. If you think about and practise this way of thinking and learning, you may avoid approaching tasks in unproductive ways.

The Three Questions: What, How and Why?

The most important thing you can do when you first confront a challenging problem is to lay down your pens, pencils and other tools, put your hands at your sides in a comfortable position, relax, and *read the problem through carefully*.

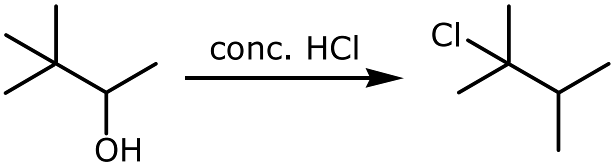
This sounds obvious, and you may think that this is what you have been doing all along, but I am quite sure that most university students in fact are *not* doing this in the way that I mean. *Reading is not a passive experience in which information flows from the page into your head.* Simply perceiving the words and images on a page does not necessarily lead to understanding their information content. When I talk about reading, I mean that you should engage in a dialogue with the text before you – the text makes a statement, and you respond with questions that must be answered:

- What does that mean?
- How is that related to other things I know?
- Why should that statement be true?

In fact, the thing that messes students up the most in problem solving is failing to grasp what the question actually says. There is a lot of information embedded in a problem, but it won't jump up and announce itself to you. You have to look for it. The solution to the problem is almost always contained within the problem itself, so it is worth your time to stop writing and try to find out what the problem has to say to you.

For this purpose, I suggest three questions, in the following order: **What**, **How**, and **Why**. Most students start out with How and Why, but I want to show you that What should come first, and is probably the most important question you need to answer in seeking a solution to a problem.

Example: An organic reaction mechanism



Step 1: WHAT is happening in this reaction?

You should look closely at all components of the reaction: the reactant, the product, and the reagents, solvents and conditions. Note down (either on paper or mentally) all the properties you can think of for each item. At this stage, nothing is too trivial, because you don't yet know enough about the problem to decide what matters and what doesn't. You might make a table to summarize what you find.

Starting Compound	**Reagents/Conditions**	**Product**
An alcohol	Aqueous hydrochloric acid	An alkyl chloride
Formula $C_6H_{14}O$	HCl is a strong acid	Formula $C_6H_{13}Cl$
Contains a quaternary carbon centre (next to alcohol group)		No quaternary centres; note location of methyl groups differs from that in starting compound
Alcohol is secondary		Halide is tertiary

It is important to note what *isn't* present as well. For example, you will observe that the reaction is not balanced as written. Organic chemists are a bit lazy, and tend to focus their attention only on the main organic product of a reaction. In this case, there is another product: H_2O. If you see a reaction that is obviously not balanced, you *must* deduce what the missing fragment(s) is(are) before going any further.

You should next *map the product atoms onto the corresponding atoms in the starting material and/or the reagent(s)*. Here, you begin to use more of your chemistry knowledge, but much of this analysis is simply connecting things in one place with similar things in another place. Obviously the chlorine in the product came from the reagent, and it should also be clear that the water arose from the OH group. You can reasonably suppose that the four contiguous carbon atoms in both starting compound and product are identical. Note that at this stage, you should not think about *how* things could happen – just focus on identifying what has happened.

It should now be clear to you that the chlorine occupies a space in the product that had been held by a methyl group in the starting compound. Likewise, in the product the methyl group is where the hydroxyl had been.

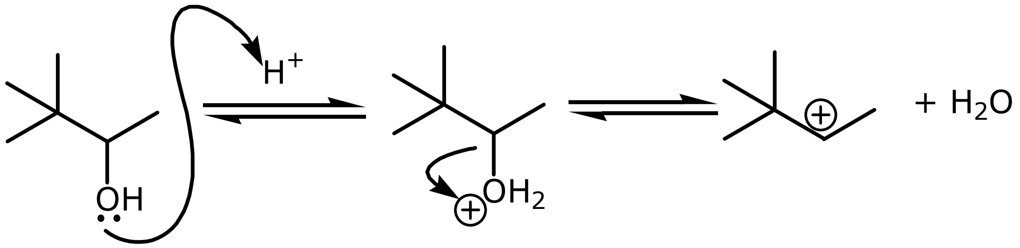
Step 2: HOW could these changes occur?

At this stage, you can begin to think about the reaction in mechanistic terms. You have identified some specific things that your reaction mechanism must address:

1. What causes the OH group to leave the starting compound as water?
2. How does a methyl group move from one carbon to an adjacent carbon?
3. How does the Cl atom become attached to the product?

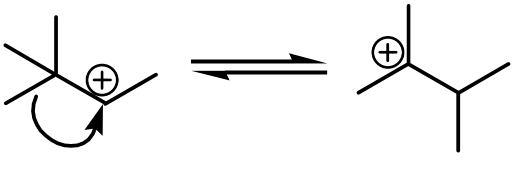
You should still keep your attention focused on the specifics. Solve each part of the problem as much as possible before worrying about how it will all fit together. You can keep from becoming confused or intimidated by all the things you don't (yet) know, because you are thinking about the smaller pieces that you actually know quite well.

So, we know that the reaction conditions are *acidic*. We also know that the alcohol OH group is being transformed into H_2O. Finally, we know that the oxygen of an alcohol has lone-pair electrons and thus can act as a Bronsted base. This suggests that our mechanism should start by *protonating the OH*, and continue by loss of water to form a secondary cation. We have seen many examples of this kind of process, so this makes sense.

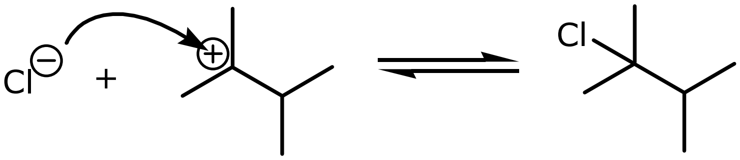


We have achieved a reasonable mechanism to explain the first point in the problem. We do not necessarily know that what we have written is correct, or that it will fit in with what follows, but that should not worry us at this stage. What we have written is self-consistent. If it proves unworkable in the overall picture, we simply need to re-examine it.

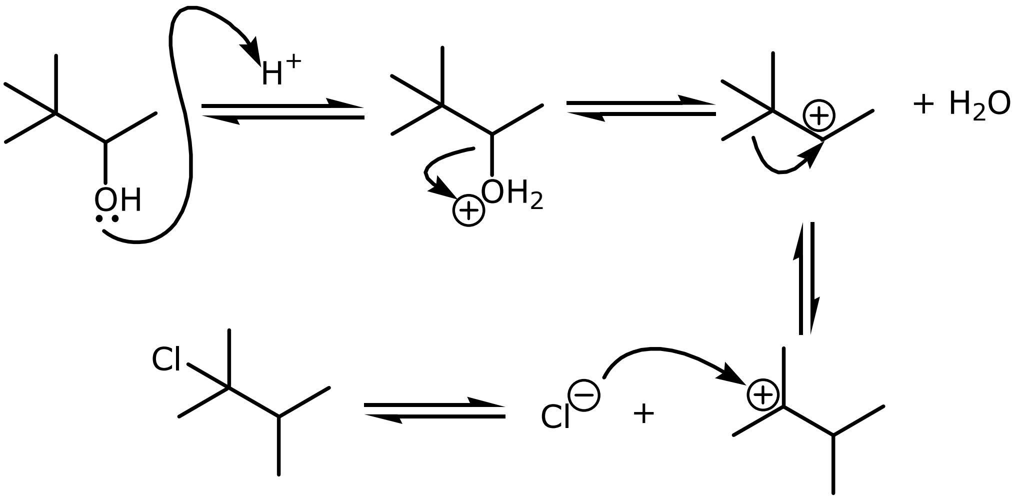
The cation that we have formed in the scheme above becomes the starting material for the next step, which is either the addition of the Cl atom, or the movement of the CH_3 group. I hope it is clear to you that the methyl must move before the Cl can be introduced. You know that alkyl or hydrogen groups adjacent to a cation can migrate in a 1,2-shift, provided that this leads to a more-stable product. Does this apply here?



It does! Methyl migration leads to a tertiary cation, which we know will be more stable than an isomeric secondary cation. Moreover, you can see that we have now formed the carbon skeleton of our product, and we have a carbocation at the site where we must introduce chlorine. This is very useful, because we also know that chlorine is present in our reaction mixture as *chloride ion* (Cl^-).



We have formed our product, in a step that looks quite familiar. Now, we can assemble all the pieces of our solution, and see whether they make sense together. I think you will agree that this looks pretty reasonable.



The important thing to realise is that even if a part of it had not looked right, you would *not* necessarily have to start over from scratch. If all the other steps appear to be reasonable taken independently, it makes sense to focus on the one that seems wrong, and to seek an alternative. There are often alternatives. Don't worry now about why a process follows one pathway rather than another. Just figure out what pathway it is following. The explanations will come later.

Step 3: WHY would this occur?

You don't always have to address the question of why something occurs, when responding to a problem, but I strongly recommend that you do so when practicing and studying. You will learn much more from trying to link your specific answer to your general knowledge of chemistry, and you will find that building a coherent explanation is a way of checking your work.

For this problem, the question is "why does 3,3-dimethyl-2-butanol react with concentrated hydrochloric acid to form 2,3-dimethyl-2-butanol and water?" In response to this question, you might cite the following reasons, most of which follow from the arguments we made while figuring out *how* the process might occur:

- Once a secondary cation is formed, migration leads to a much more thermodynamically stable tertiary cation isomer.
- It is reasonable to suppose that the three CH_3 groups attached to a single carbon atom in the starting compound might be a bit sterically crowded. In the product this crowding is relieved.
- Chloride ion (an anion) is a better nucleophile than water (a neutral).

What did this example show us?

The specific chemistry of this example is not important. Many of you probably saw right away what the mechanism had to be, because it is straightforward organic chemistry. The important thing in this sample problem is to see that *once we knew WHAT was happening, the HOW followed quite logically*. As well, once we had answers to the What and How questions, it was much easier to address the deeper issue of *WHY*.

You should also note that when figuring out WHAT needs to be accomplished, you are not really using very sophisticated chemistry. In many problems of this kind, you don't need any chemical knowledge at all to identify what has changed in going from starting point to product. The job may be as simple as saying "this letter C was attached *here* but now it is attached *there*", or "there was a line (a bond) between *these* two carbons, but now there is not. A new line exists between *those* two carbons instead."

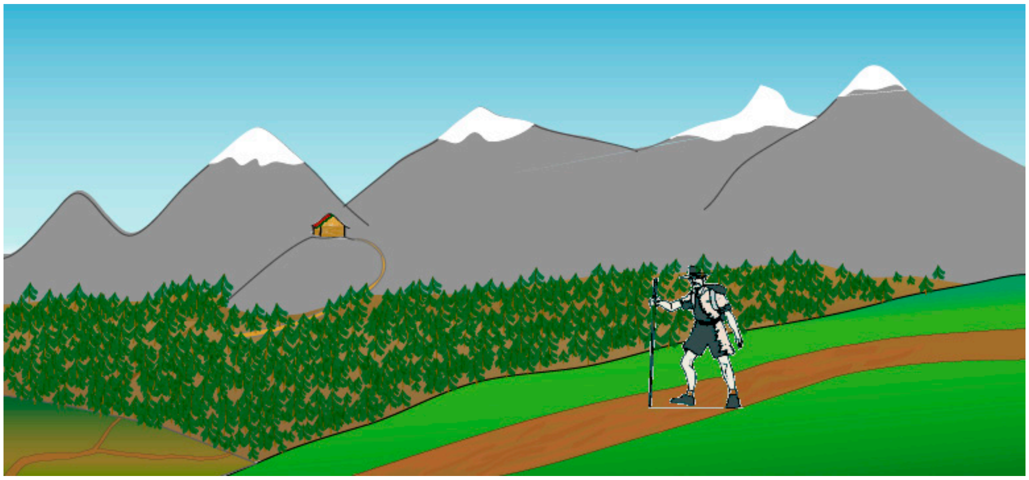
The idea is to reduce a complex task into a series of simpler jobs that are less intimidating. Try to define your sub-tasks very specifically – it is much easier to do a job when you know exactly what needs to be done. At the end of each sub-task, stop and ask yourself "Where am I? Have I moved closer to my goal, or further away? Can I see another path leading onward from where I am now?"

You don't need to see all the details of each stage in your solution right from the outset. In fact, sometimes you might not be able to identify all the "what" items when you start. If you can see the first few things that need to be done, it is a good idea to begin working with them. When you have worked your way to the end of these steps, take another look around. Treat the remainder of the problem as if it were a new question – ask WHAT must still be accomplished, and then address HOW to do this. It may turn out to be much clearer how to reach your ultimate goal from halfway down the road than it was when you stood at the beginning of the adventure.

Problem solving as exploration

The metaphor of exploration is very useful in looking at the problem we just solved. At the outset, we stood back and looked at the landscape in front of us. We could see our objective (the product) and we believed that there was indeed a pathway between where we stood (the starting material) and our objective. However, we could not see that pathway yet – perhaps it led through a thick forest or behind some hills. What we could see was that there were several paths before us that led in the right general direction.

As we ventured into the forest of information contained in the problem, we began to see more of the pathway. The general landscape also became clearer as we progressed, until we reached a point where we could look at the entire road and see that it did indeed lead from our starting point to our objective. Our journey of exploration was complete, but like any explorer it remained to finish making a map of our discoveries, so that others could follow. This map was the overall reaction scheme that we finally wrote down as our answer to the problem. Check your map to make sure it accurately and completely represents the path you discovered and you are done!



Preparing Yourself

Before setting out on a journey into the unknown, a wise adventurer will be sure to equip herself with all the tools she can imagine needing. She needs to know just what equipment she has with her, and that it all works properly. Above all, she will take care to organize all her equipment so that it is ready to use when required. Obviously, a similar approach will be useful in setting out to be a problem solver. You must have a certain amount of accurate factual knowledge with which to build solutions to problems, but if the knowledge is poorly organized, it will not be very useful to you.

If you regard information as a series of isolated facts to be filed away in your memory, it is almost certain that you will have great difficulty using any particular part of your knowledge to solve a new and challenging problem. *When you are learning a new subject, the key is to forge connections between the new information you are receiving, and things you already know.* You must also work at finding links among the new facts and concepts. Ask yourself "What is this new idea similar to?", and "In what specific ways are these ideas related?". By seeking connections among things you are learning, you are doing two things:

1. You are creating a mental "filing system" that will help you to find related ideas when you need them.
2. You are training yourself to see analogies.

The ability to perceive similarity or analogy is crucial to successful problem solving. Although to a beginner it may seem that there are infinitely many possible problems, in fact you will find that situations tend to fall into patterns. Often your analysis of “What” is happening in a problem situation will remind you of something you have seen elsewhere. Even if the similarity is incomplete, you have a great advantage if you can model your response to a new challenge on something you have previously figured out.

If you constantly seek analogies among the new things you hear in lectures or read in your textbooks, you will find that you get better at identifying similarities in things. It is equally important to be able to detect differences. You have probably already discovered that things may appear similar on the surface, but may differ substantially when examined more closely. While studying, don’t simply memorize facts – catalog the similarities and differences among the facts as you go along.

How do you actually do all this? You must remember that reading is *not* a passive experience. If you expect that information will flow spontaneously from the pages of your textbook or your notes into your head and neatly file itself, you are in for a big disappointment sooner or later. You must try to establish a *dialogue* with your textbook.

This is not as crazy as it might sound. Look at it this way: your book makes an assertion of fact. You respond “Why is that so?”. Now, the book can’t speak, so it is up to you to look for the book’s answer. It might be in the very next sentence, but on the other hand, the explanation might actually be in something you read in a previous chapter. You must provide the book’s reply to your question either from your memory of what you have read or by seeking the relevant material in the book.

Another way you have a dialogue with your textbook applies to the examples that a book provides. When a chemistry book shows an example of a reaction, the example itself is much less important than are the principles that it embodies. These principles may not all be obvious, however. You should look carefully at all examples, and work through what they show as if it were a problem. You need to *deduce* the message(s) of the example by a kind of question-and-answer approach. This is where the real learning occurs.

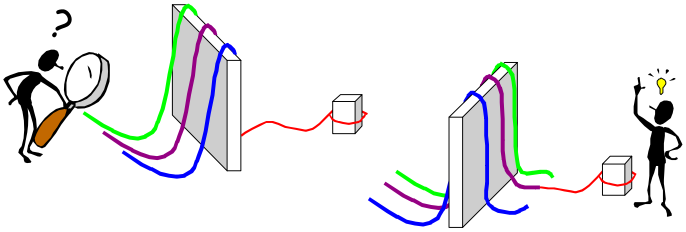
Finally, there is an important dialogue that should occur whenever you do a practice problem from your text. On completing a problem, most of you will check to see if you got the correct answer. If you didn’t you probably set about trying to figure out where you went wrong, and this is of course exactly what you should do. But, what if you *did* get the correct answer? I would bet that most students simply move right on to the next problem at this stage. After all, you got it correct, what more is there – right?

Wrong! When you complete a practice question, you should sit back and ask some questions:

- "What was that question about?"
- "What principles did I use to come to the correct solution?"
- "What problem-solving strategies did I use?"
- "Were there any points that I was not sure about while solving the problem – if so, are they now clearer?"

I suggest that unless you actually do this analysis, you probably have learned very little from the practice question, and you are unlikely to remember what you did at the time when you really need it.

Working Backwards: Another Useful Strategy

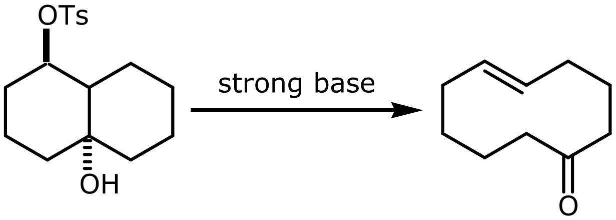


An explorer usually can't work backwards from his goal if he encounters problems going forwards. But a problem solver often has the option of starting from the end of a problem as well as from the beginning.

This type of analysis is especially useful in organic reaction mechanisms, or in the "explain what is happening and why" type of question. It is also absolutely essential in "propose a multi-step synthetic route" questions, and indeed in this context "working backwards" from the target is usually the best possible approach – it is called "retrosynthetic analysis".

Often when you are stumped by a problem, it is only one step somewhere in the middle that is causing the difficulty. You can see a few possible ways of beginning, but you can't see how any of them connect to the goal. In this situation, if you can work backwards from what you need to achieve, you may be able to perceive which starting option is best.

Example: Another mechanism



NB: OTs is shorthand for the O-toluenesulfonate group ($OSO_2C_6H_4CH_3$). The starting compound can be regarded as an ester of toluenesulfonic acid.

In a question like this, it is helpful to think backwards from the product *and* forwards from the starting compound.

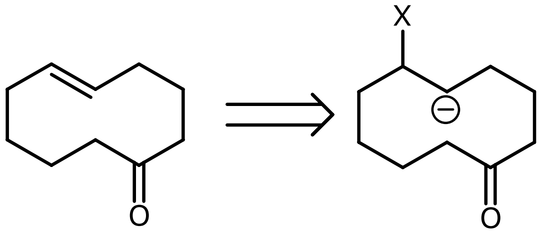
Step 1: WHAT is happening here?

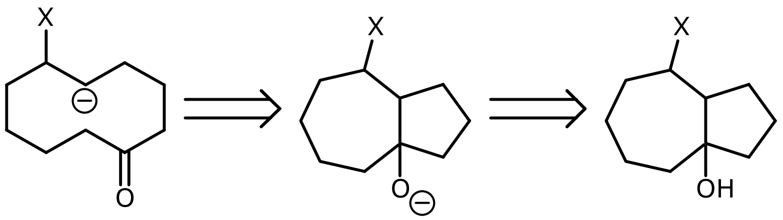
Starting Compound	Product
$C_{17}H_{24}O_4S$	$C_{10}H_{16}O$ (loss of $C_7H_8O_3S$)
Ten carbons in two fused 6-membered rings (a *decalin* ring system).	Ten carbons in a single cyclodecenone ring. **The bond across the ring has been broken!**
Contains a good leaving group (OTs) which is adjacent to the bond across the ring	Leaving group is gone but an alkene has been formed.
Contains a tertiary alcohol, which is directly attached to the bond across the ring.	Contains a ketone.
Counting around the ring, the alcohol is separated from the OTs group by *three carbons in one direction, and by five carbons in the other.*	Counting around the ring, the ketone is separated from the alkene by *three carbons in one direction*. Counting in the other direction, the other alkene carbon is the *fifth* carbon away.

We can also see that the reaction conditions do not include any obvious oxidizing agent. All we have is a simple base.

Step 2: HOW could these changes happen?

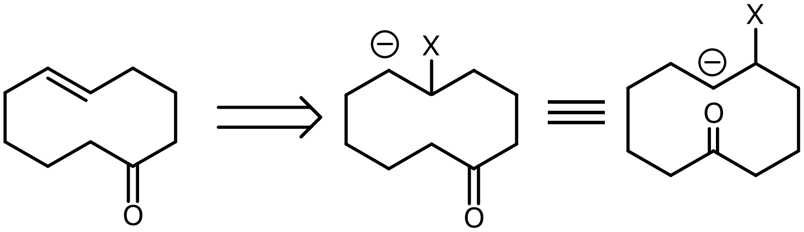
Now is the time to think backwards. You see an alkene in the product and you know that one good way to make alkenes is by an *elimination reaction*. You have a good leaving group on the starting material, so an elimination is certainly possible. Let's assume that the alkene in the product was formed by an elimination, and work backwards from there. We will simply use "X" to represent the leaving group for the time being. You can see that this leads us to a carbanion. Now, let's assume that this carbanion was created as the product of another step. Thinking backwards (remember that all reactions are in principle reversible) we could imagine this anion attacking the carbonyl, *to make a tertiary alcohol*! We see that this idea gets us back to a fused ring system containing a leaving group and an alcohol, *but this is not the correct starting structure*. We have a seven-membered ring fused to a five-membered ring, and not the pair of six-membered rings that make a decalin system.

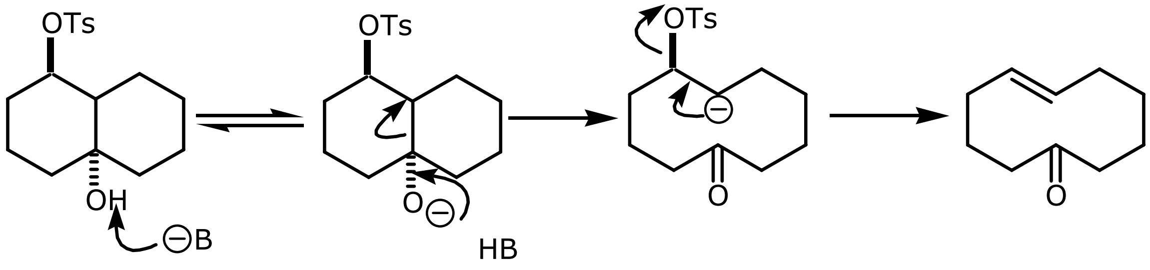


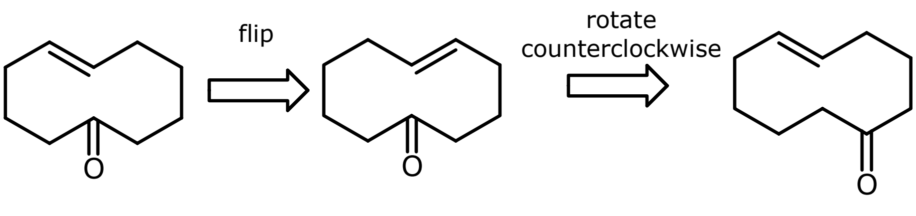


Now wait! A common student error is to abandon an entire concept when a problem arises, before they have examined the situation in detail. Don’t let this happen to you. Look at what we have found – we have a concept that gets us back to something very similar to our desired starting material. It has the right functional groups. It simply puts the bond across the ten-membered ring in the wrong place.

But why did we assume that the elimination occurred as we wrote it above? This was really an arbitrary choice, suggested by the way in which the structures were written out. What if we wrote the elimination the other way around? At first this doesn’t look helpful, but let’s just re-write the structure by rotating the ring around in a clockwise direction, like a conveyor belt on a pair of rollers. Doesn’t this look better? Now, if we join the anion to the carbonyl we will get the tertiary alcohol, and the right type of rings. The reverse analysis takes us through the conjugate base of the alcohol, which tells us that going forwards, the first step is deprotonation. The product might not look right at first, but if we simply re-draw it in a new orientation we can see that it is correct.







Step 3: WHY did this occur?

You might wonder about the formation of the secondary carbanion, as a result of the alkoxide collapsing to a carbonyl. It seems counter-intuitive because it is transforming a weaker base (alkoxide, pKa ~ 17) to a stronger base (carbanion, pKa ~ 50). But consider the possibility that the last two steps of the reaction might be *concerted*. In this case, the carbanion is never actually formed: as the central C-C bond is cleaved, the electron pair is pushed directly into forming the pi bond by expulsion of the toluenesulfonate. This would make thermodynamic sense, since the leaving group anion is a much weaker base than the alkoxide (pKa ~ -6.5).

There are other aspects of this problem that go beyond the scope of an introductory organic chemistry course, and which really have no bearing on the question of logical problem solving. We will therefore move on without developing a response to the "why" question any further.

What did this example teach us?

In this mechanism problem we saw that working backwards from the endpoint of the situation under study could clarify what might otherwise be very hard to understand. Notice how we asked "how might this structure have been formed", and then looked at the options to choose a pathway that seemed to fit the overall problem.

Another important lesson was how to respond when things don't appear to be working out. *Do not abandon a possible solution before you have examined all probable variations on its underlying concept.* We saw that although the specific pathway we had initially chosen was incorrect, the fundamental chemistry we were thinking of was what we needed to solve the problem. When you encounter a setback, you must step back slowly and examine where you are in solving the problem. Don't drop what you have developed and retreat all the way back to your starting point. Most likely you have at least some parts of the solution correct, so the logical thing to do is to move back systematically, and look for the place where you took a wrong turn.

Summing up

Problem solving situations arise in almost every aspect of life, and if you can learn how to solve organic chemistry problems logically, you will have learned skills that are readily exported to other activities. I hope that the idea of problem solving as a process of exploration is clear to you now. This idea is central to my own approach to learning, teaching and research, and it may work equally well for you. I don't expect problems to yield up their secrets easily, but I know that most complex problems are actually the sum of many relatively simple issues. When I work on such a situation, in chemistry or in any other area, I look for openings by a process of exploration, and then widen my approach when I find something that seems relevant to the overall question. Usually, a little bit of careful thought, along with discipline to keep you from jumping to unwarranted conclusions, will give you the start on the path to a solution.

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"Armed with a telescope and sextant" from the website Cnut online(Cnut is an electronica/dance band from Glasgow Scotland – check out their music. Thanks to the band for permission to use the cover of one of their CDs in this document)

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