

## SELECTED ANSWERS

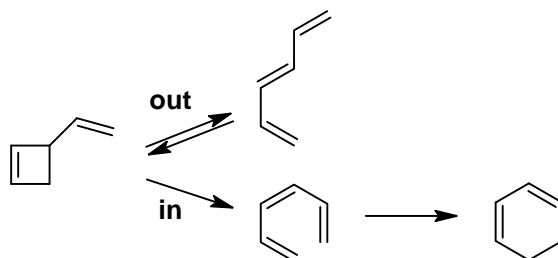
Your answers were generally correct. Still, I saw a number of minor things that you should attend to.

Since these are (for the most part) minor issues, I don't want you to hear the wrong message. When you approach a problem and need to brainstorm, don't be overly critical. The important thing is to get some ideas out there without being too judgmental. However, once you move on to writing down your answer, you must be punctilious. Careful drawings help others understand you. Careful drawings also help you spot flaws and gaps in your thinking.

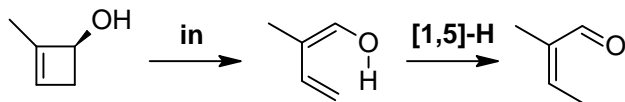
Missing labels:

- Cycloaddition? Provide [m+n] and show product stereochemistry.
- Sigmatropic rearrangement? Provide [m, n] and show product stereochemistry.
- Electrocyclic? Provide CON or DIS and show product stereochemistry.

1a. Allowed ring-opening is conrotatory, but if the vinyl group spins outward, the result is a *trans*-triene that cannot close to cyclohexadiene (top pathway). The vinyl group must spin inward (less plausible, but oh well) and generate a *cis*-triene (bottom pathway).



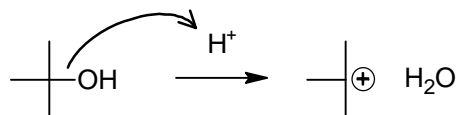
1b. Outward vs. inward is important here too. If inward rotation of OH occurs, the resulting dienol can tautomerize by a [1,5]-H shift (shown below). However, this leads to the wrong product isomer (I gave you a product with *cis* methyl groups, but perhaps I copied the problem down incorrectly?).



In fact, separate experiments show that OH/OR groups normally rotate outward. This makes tautomerization by [1,5]-H shift impossible. A pair of acid-base reactions is the only alternative. Either deprotonate O to make an enolate and reprotonate on C, or protonate C to make an allylic O-stabilized carbocation and deprotonate O. Neither of these pathways explains why one gets a product with *cis* methyl groups, but they don't rule out this possibility.

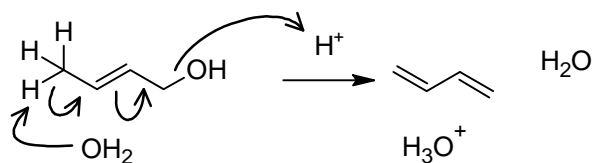
2. A variety of problems appeared here. I will illustrate only a few points, so this list is not complete. If you have questions about your mechanisms (or the notes I made on them), please come see me.

*Undesirable short-cut #1 – Combining two steps.* A detailed mechanism shows every intermediate. Mechanisms in research articles don't always play by this rule because page space is expensive, but expense is no object on a homework assignment.



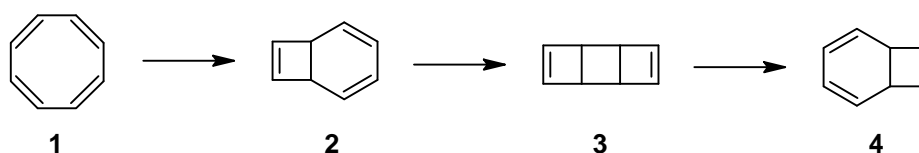
The mechanism shown above is usually incorrect. You should draw *two* steps: protonation of oxygen to make  $\text{ROH}_2^+$  followed by loss of water. Also, the drawing seems to say that alcohols are basic by virtue of easily shared CO bonding electrons. This is entirely wrong. It is the lone pairs on oxygen that are responsible for basic behavior.

*Undesirable short-cut #2 – Termolecular reactions.* Students sometimes resort to highly improbable termolecular steps out of ignorance, i.e., they don't realize that the entropic penalty makes such collisions highly unlikely. Then there is the attempt to save space by combining two collisions in a single step. Whatever the reason, avoid termolecular reactions.



The mechanism shown above combines two errors: protonating a CO bond pair and an extremely improbable termolecular reaction.

*Undesirable drawings of various sorts: unproductive side reactions.* Take a look at this:

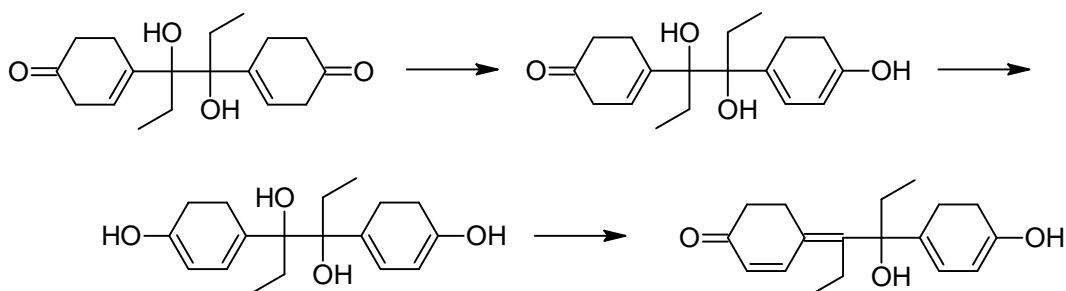


The two steps from **2** to **4** don't actually accomplish anything because **2** and **4** are the same. These steps are unproductive and should be omitted.

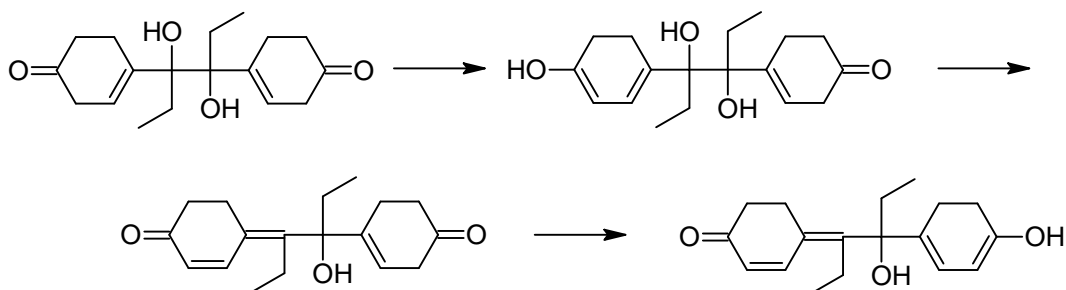
*Undesirable drawings: high-energy non-viable intermediates.* **2**  $\rightarrow$  **3** is also problematic because the strain energy of **3** is very high. Unless very high temperatures are used, **3** won't be a viable intermediate.

Another example I saw of an unrealistic intermediate: a bis-enol. Energy must be stored inside a molecule in order to convert a ketone into its enol. Even more energy is required to do this twice.

The following sequence (I have taken some short-cuts and left some steps out) shows: diketone  $\rightarrow$  enol-ketone  $\rightarrow$  bis-enol  $\rightarrow$  enol-ketone + water. The ending point is a desirable species, but its precursor is a bis-enol, so this pathway is extremely unlikely.



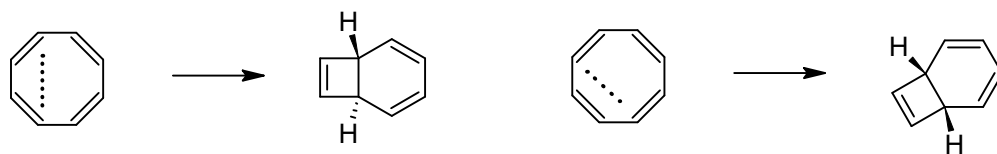
A less energy-demanding and, therefore, more plausible pathway is shown below:



*Undesirable drawings: collisions between short-lived intermediates.* Timing is everything. I have heard that certain butterflies emerge from their cocoons with just 24 hours to live. If they are lucky, they find an equally short-lived partner, mate, and lay their eggs, before being eaten or collapsing from exhaustion. Reaction intermediates have much shorter life spans than butterflies, often just a microsecond or less. During this period they are bombarded thousands of times by surrounding molecules. Very few, if any, of these collisions involve other short-lived species. Therefore, your mechanisms should not combine two short-lived intermediates in a single step.

The bis-enol problem can be viewed as a “collision” of two short-lived intermediates.

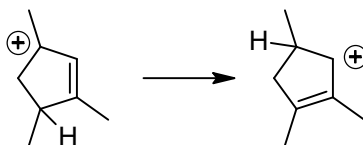
*Undesirable drawings: hidden electronic problems.* One of my favorite optical illusions is a drawing that looks like one thing the first time you look at it, and something completely different the next time. The conversion of **1**  $\rightarrow$  **2** is the chemist’s version of this optical illusion. Look at it once and you may see a four-atom electrocyclic reaction (below left). Look at it again and you may see a six-atom electrocyclic reaction (below right).



Unlike an optical illusion, only one of these views is likely to be correct. A four-electron electrocyclic reaction must be conrotatory. This yields a highly strained *trans*-fused ring system.

A six-electron reaction, on the other hand, must be disrotatory. This yields a far more stable *cis*-fused ring system. In the absence of other evidence,  $1 \rightarrow 2$  should be regarded as a six-electron reaction.

A suprafacial [1,4]-H shift presents a similar problem: the reaction is almost certainly suprafacial and must be forbidden (4e, Huckel). A step-wise pathway (cation  $\rightarrow$  diene +  $H^+$   $\rightarrow$  cation) avoids this problem.



3. Everyone did the math correctly. Rationales varied. The most straightforward answer is “steric repulsion raises the energy of the methyl-in transition state.” It would be *nice*, however, if you could point out something that indicates steric repulsion. It can’t be energy because this would make your argument circular: higher energy transition state because of repulsion, repulsion confirmed because higher energy transition state.

There are many ideas you can pursue:

- Steric repulsion should lead to a perturbed geometry (and it should be possible to link repulsion logically with geometric perturbation). Interatomic distances? Angles? Dihedral angles? Usually a reference (unperturbed) geometry is needed.
- Structural analogy. Methyl-in leads to the *cis* diene and methyl-out leads to the *trans* diene. If you can show or claim that the *cis* diene experiences more steric repulsion then you might infer more steric repulsion for the methyl-in transition state.