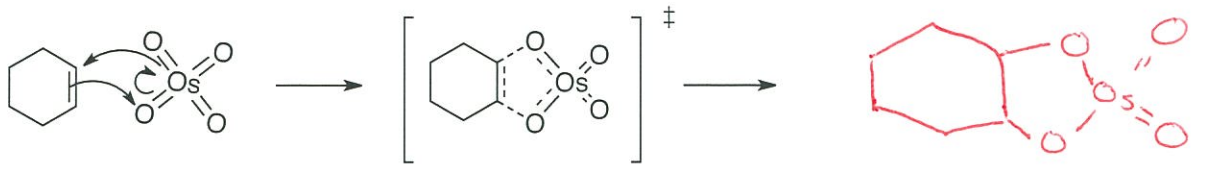
CHAPTER 8. ALKENES: REACTIONS AND SYNTHESIS

Dihydroxylation. Oxidation by OsO_4 to a *cis* vicinal diol

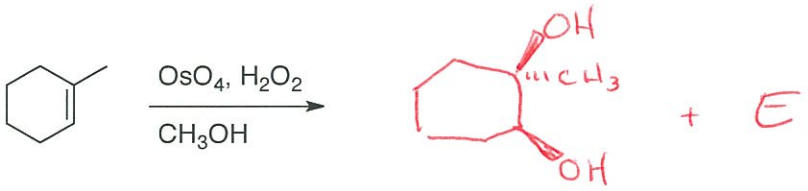
- concerted [4+2] cycloaddition of OsO_4 to form 5-membered cyclic osmate
- oxidation of cyclic osmate results in formation of *cis*-diol

Connect the necessary dotted lines and draw the 5-membered osmate ring intermediate - think about stereochemistry - make sure to draw a *cis* rung juncture.

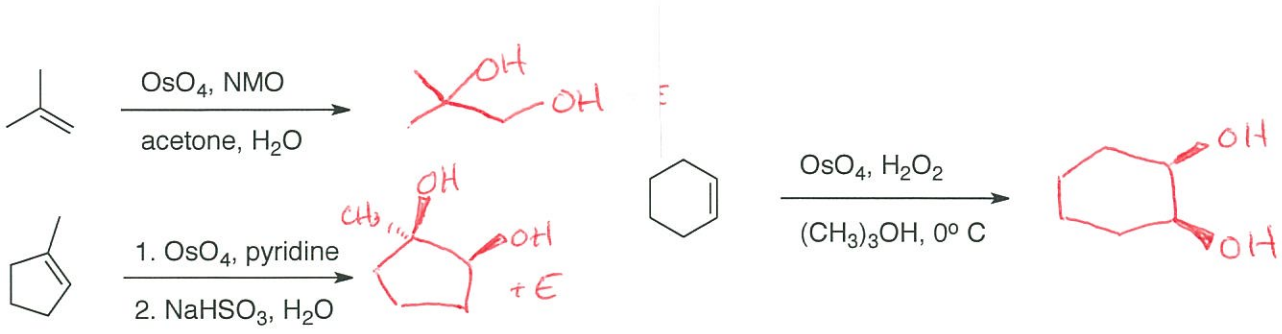


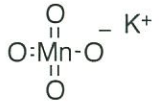
a concerted transition state 5-membered ring intermediate

These 5 membered rings dissociate upon treatment with a few oxidizing reagents; H_2O_2 and NMO are common. Draw the product(s) of the following reaction:



Here are some modifications that accomplish the same transformation. Draw the products of the following reactions:

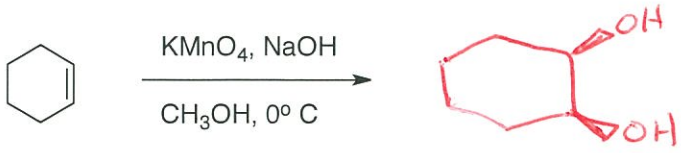




Dihydroxylation. Oxidation by $KMnO_4$ to a *cis* vicinal diol

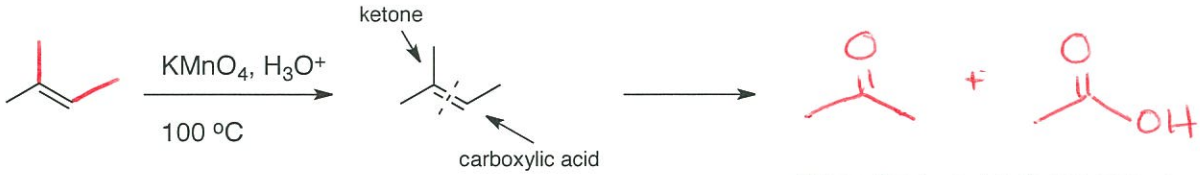
- before the use of OsO_4 was discovered for this reaction, $KMnO_4$ was used.
- concerted [4+2] cycloaddition of $KMnO_4$ to form 5-membered cyclic manganate ester.
- when reaction is run cold and under basic conditions, a *cis*-diol is formed.
- KMnO4 is generally not common for dihydroxlation, but rather oxidative cleavage (next).

Draw the organic product from the following reaction - no need to draw a mechanism.



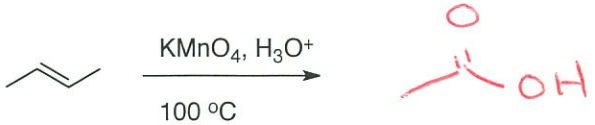
Oxidative Cleavage of Alkenes using $KMnO_4$

- When run at room temperature/warm and in the absence of base (typically acid is added), reaction results in oxidative cleavage.
- Sp^2 carbons bearing at least one hydrogen are oxidized to carboxylic acids, sp^2 carbons bearing no hydrogens oxidize to ketones.

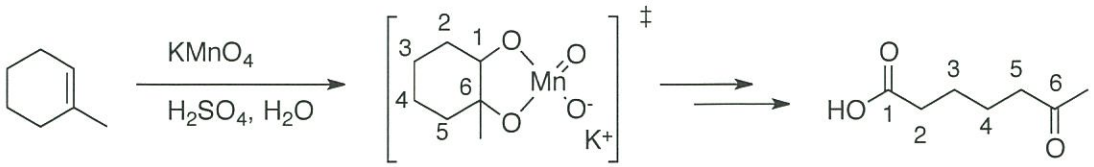


Draw the two products above.

Predict the products of these reactions:

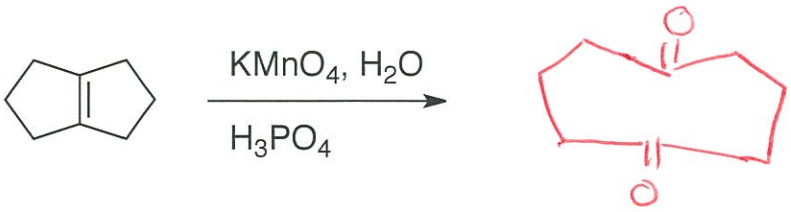


When the alkene is inside a ring, only ONE product is formed:



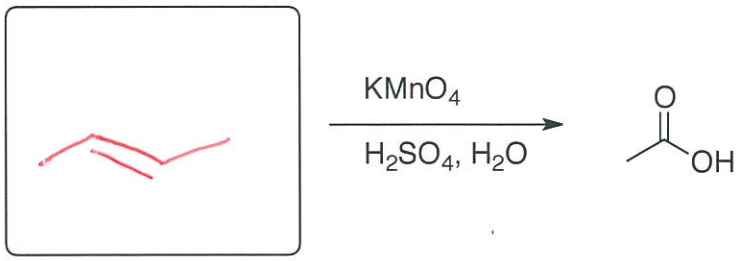
a concerted transition state

Try this one - draw the product (notice I didn't say products) of the following reaction.

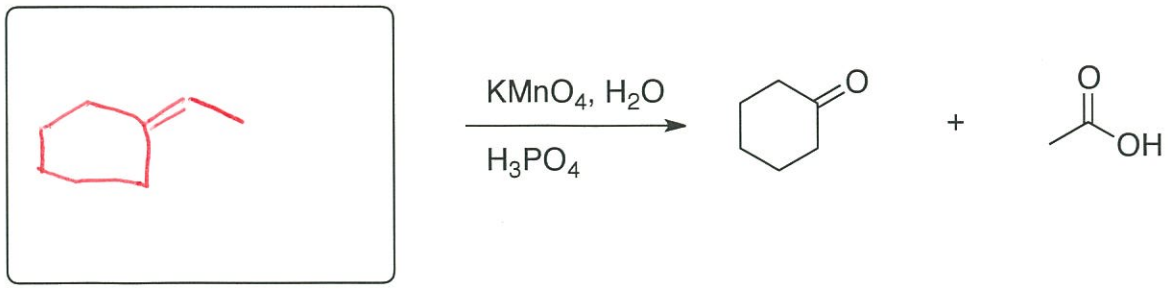


Predict which alkene, with the molecular formula C_4H_8, reacts with acidic $KMnO_4$ to give ONLY acetic acid.

- Strategy: If the starting material had 4 carbons, what two carbons were connected before the oxidative cleavage?

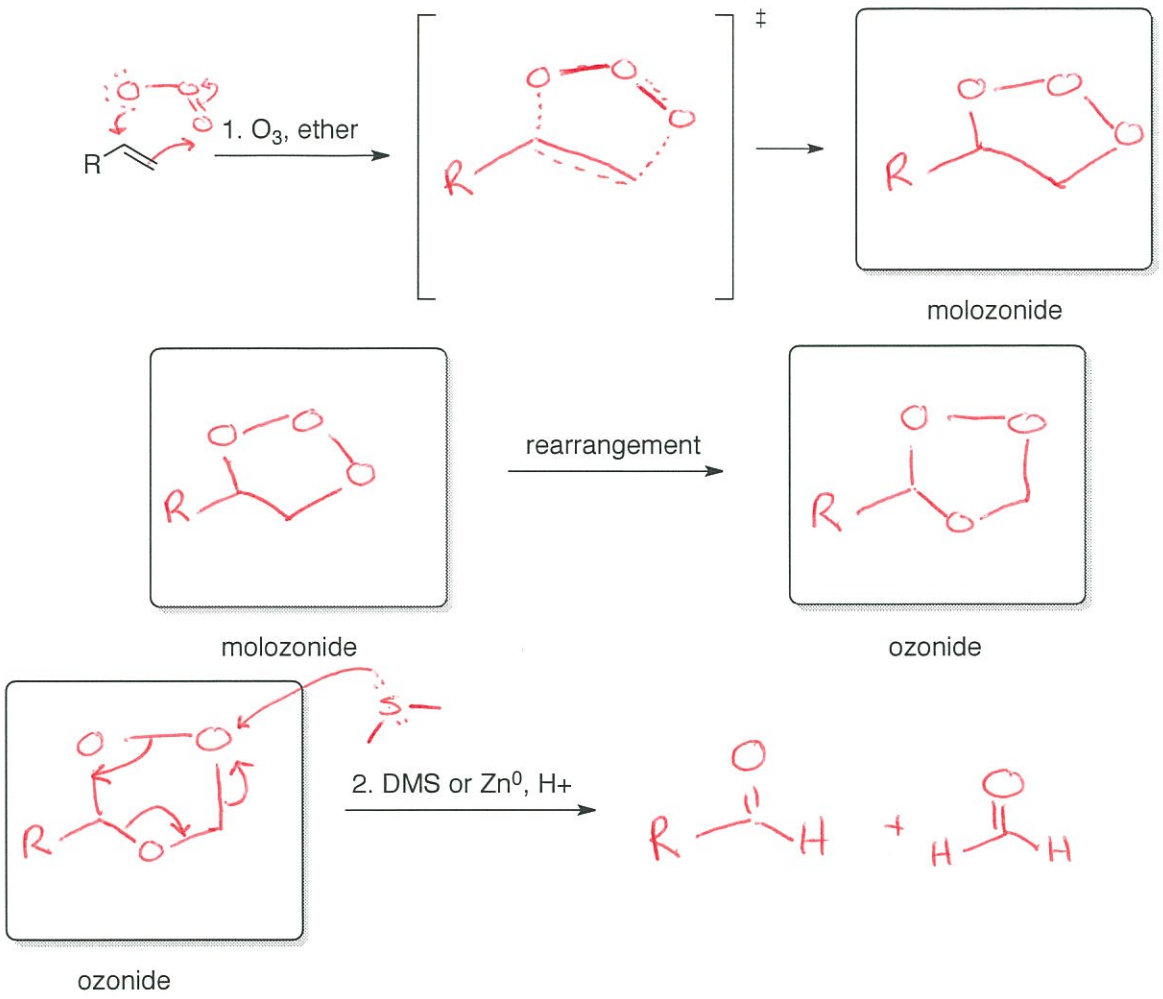


This one's a bit more challening:

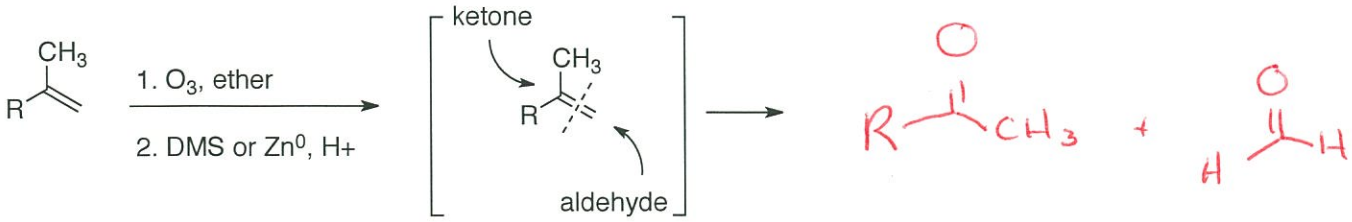


Oxidation by Ozone

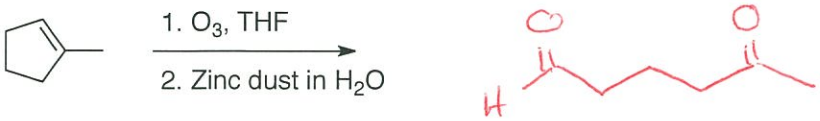
- first intermediate is a 5-membered ring (molozonide) followed by…
- rearrangement to ozonide
- reduction of ozonide by addition of DMS or Zinc (other reducing agents work, too) results in aldehydes (not carboxylic acids) and ketones



So here it is in a nut-shell: The C=C bond breaks. If the carbon bears at least one hydrogen the product is an aldehyde (unlike $KMnO_4$), otherwise it is a ketone. Draw the two products of this reaction:



Predict the product(s) of the following reactions:



What alkene produced the following molecules upon ozonolysis?