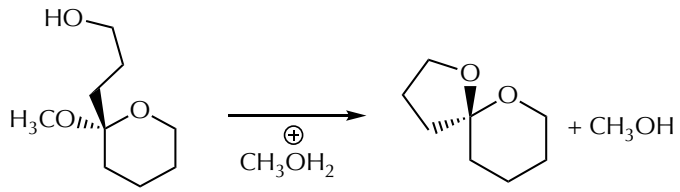
12.44 The reaction shown below involves the conversion of one ketal into another ketal using a trace quantity of protonated methanol as the acid catalyst. Methanol is generated as a byproduct of the reaction. Using your knowledge of acid-catalyzed formation of ketals as a guide, provide a curved arrow mechanism to explain the transformation. You must show closed shell resonance forms for all structures produced.

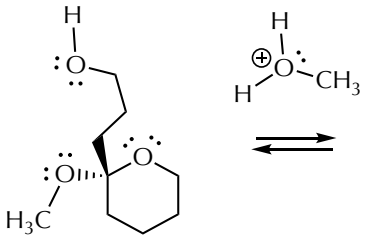
(a)

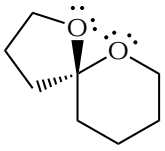


single enantiomer catalyst + enantiomer (racemic)

You should use $CH_3\overset{\oplus}{O}H_2$ as the acid and CH_3OH as the base in your mechanism.

Note: There is no water present, and the six-membered ring stays intact throughout the mechanism.





+ CH_3OH

+ enantiomer

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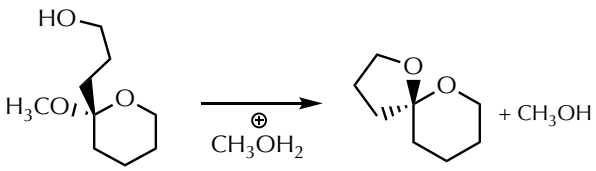

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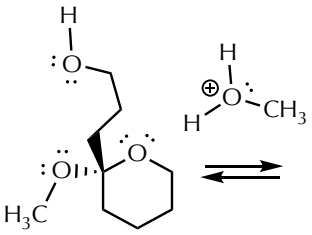
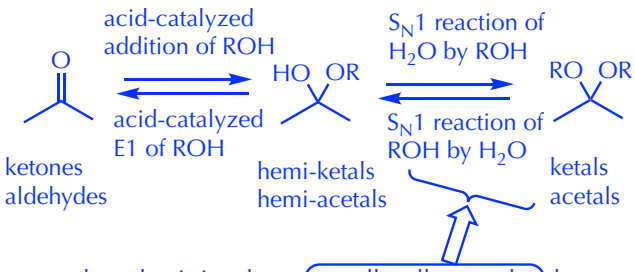


Stepping back from this problem a bit and classifying the reaction is the best strategy, but (as always) this approach relies strongly on having the prior knowledge from CHEM 210 and being able to use it. Although this is a ketal interconversion, which sounds like CHEM 215, there are two things to remember here: (a) ketal /acetal /carbonyl chemistry is best understood as a pairing of fundamental (CHEM 210) reaction mechanisms, and (b) those fundamental mechanisms are generally applicable to thousands and thousands of different specific cases. Once again, it turns out that indentification is the key decision you need to make. Arguably, if the question stated "use the S_N1 mechanism to provide the complete, curved-arrow mechanism," the question would be easier to solve even though not a single arrow was provided.

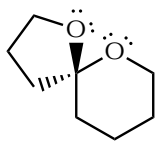
Therefore, before you start working on writing the answer to this question, your problem-solving strategy will be well-served if you look at the information presented here and can conclude "I need to apply the S_N1 mechanism here."

The problem provides information:
- explicitly says molecule is a ketal
- acid-catalyzed reaction
- tells what to use as acid/base
- the OCH_3 is lost as $HOCH_3$
- use the prior knowledge to see how it might apply, because ketal to ketal is not explicit in the scheme
- a racemic mixture forms
- no water is present

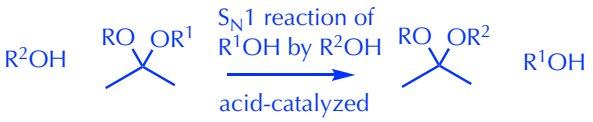
General Mechanistic Scheme



The general mechanistic scheme actually tells you what the usual chemistry of ketals is: an OR group of a ketal undergoes S_N1 reactions with water to give a hemi-ketal. There is no water here, but there is an internal alcohol that is shown doing an intramolecular substitution of the OCH_3 group. The bullet points reinforce the idea this ketal to ketal reaction is also S_N1, thus:



+ enantiomer



This analysis can and should be done before ever drawing anything.

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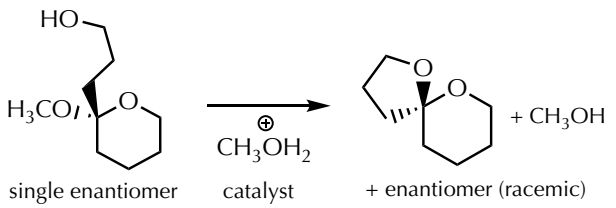

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