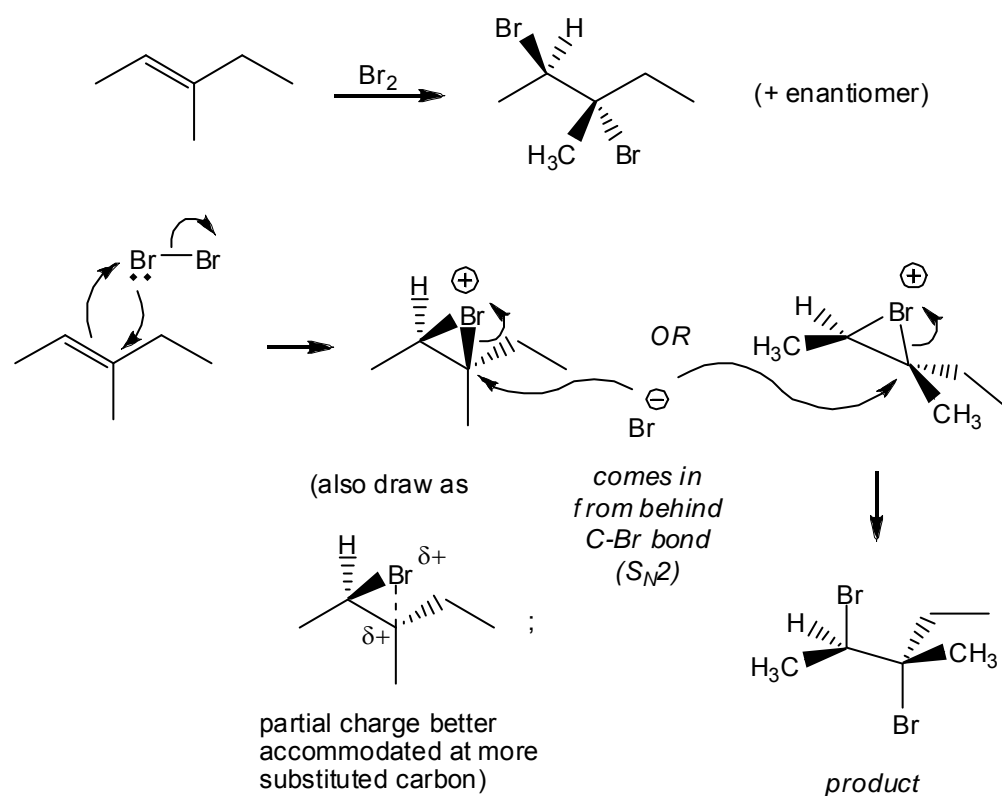
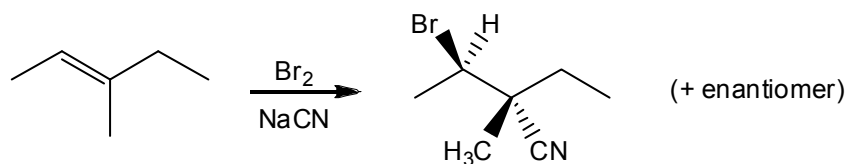


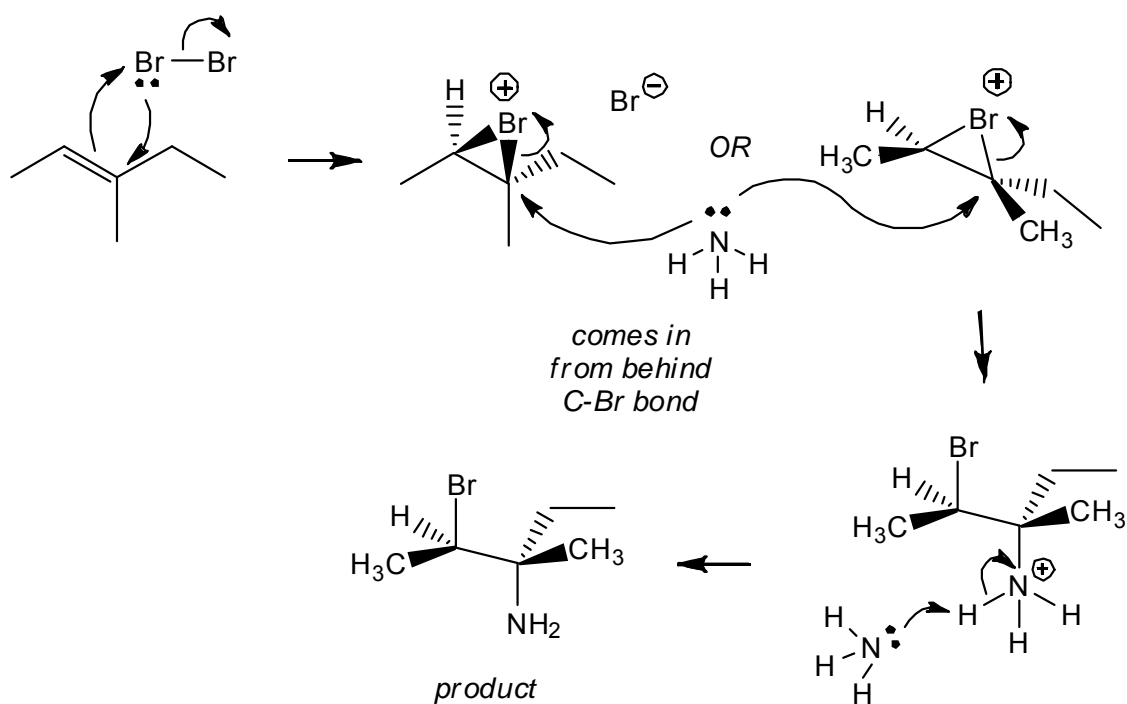
Workshop 16 Solutions
Diverted Alkene Addition Mechanisms



The other enantiomer would come from the initial bromonium ion forming from the bottom of the alkene instead of the top.



(next page)

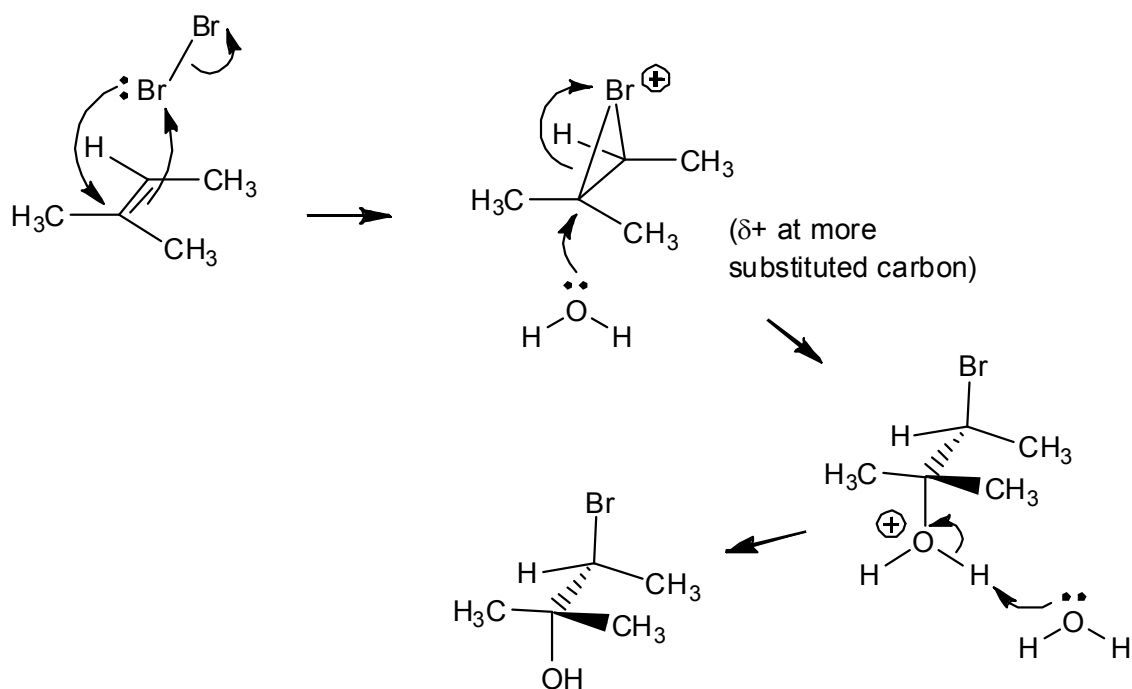
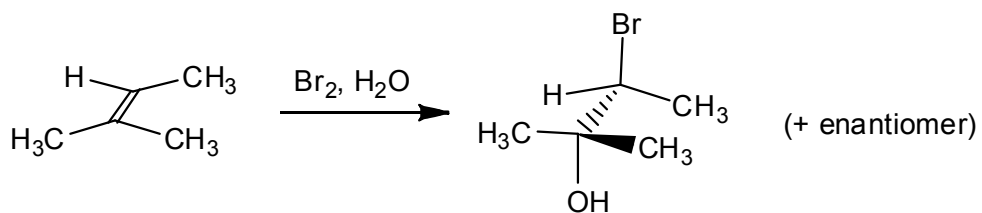


Again, the other enantiomer would come from the initial bromonium ion forming from the bottom of the alkene instead of the top, as I've shown it above.

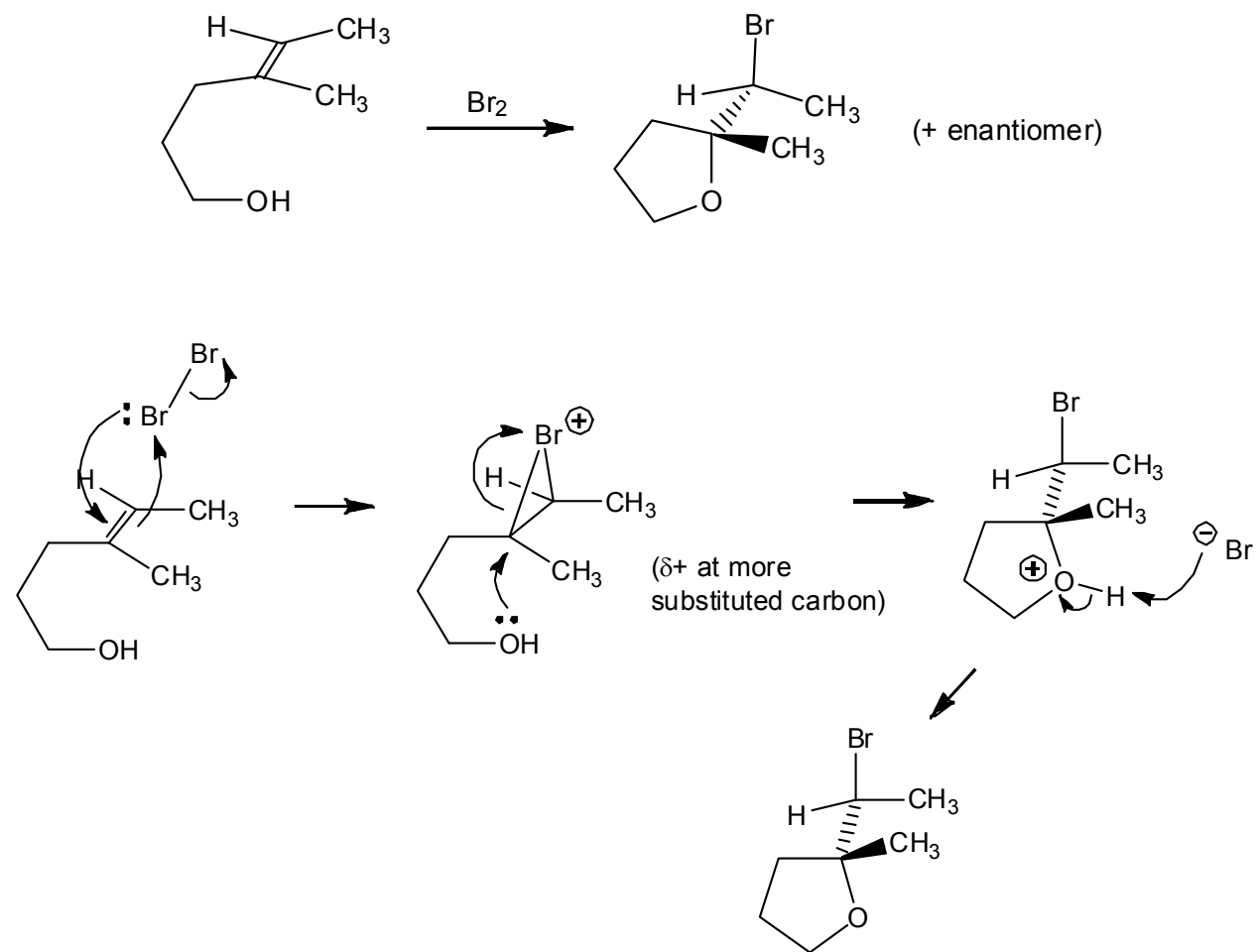
Two things that students sometimes propose, incorrectly:

Sometimes students propose that the dibromide is formed first, followed by S_N2 of ammonia on the more substituted of the two bromides. This can't explain the product. The ammonia wouldn't choose to do S_N2 on the more substituted bromide—it would choose the less substituted bromide, which would lead to the opposite regioselectivity. And the stereochemistry of the product would also be wrong, because the ammonia would substitute the -Br with inversion. This can't be the right answer.

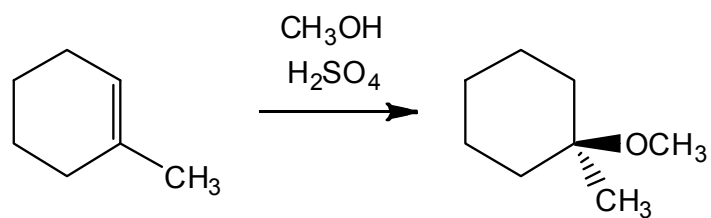
Sometimes students propose that Br⁻ deprotonates NH₃, to turn it into an ⁻NH₂ anion nucleophile. Br⁻ is an extremely weak base, the conjugate base of a strong acid (HBr). It can't deprotonate anything challenging, including a nitrogen atom that isn't very electronegative. But you don't need to deprotonate NH₃ first; NH₃ is a perfectly capable nucleophile, and can add first, and get deprotonated second, as shown above.

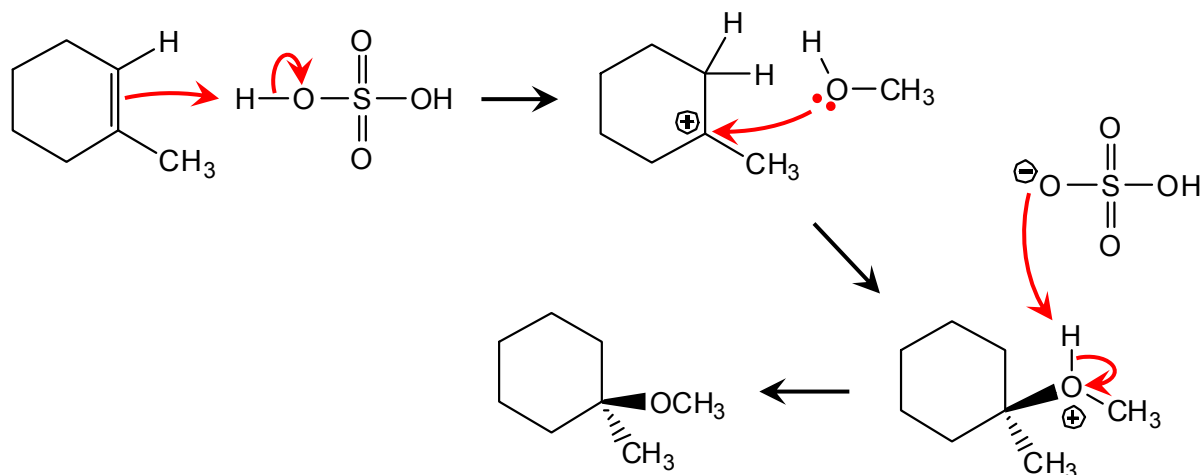


The other enantiomer would come from the bromonium ion forming on the bottom of the alkene instead of the top, and the $-\text{OH}$ then attacking from the top. We drew this mechanism in class.

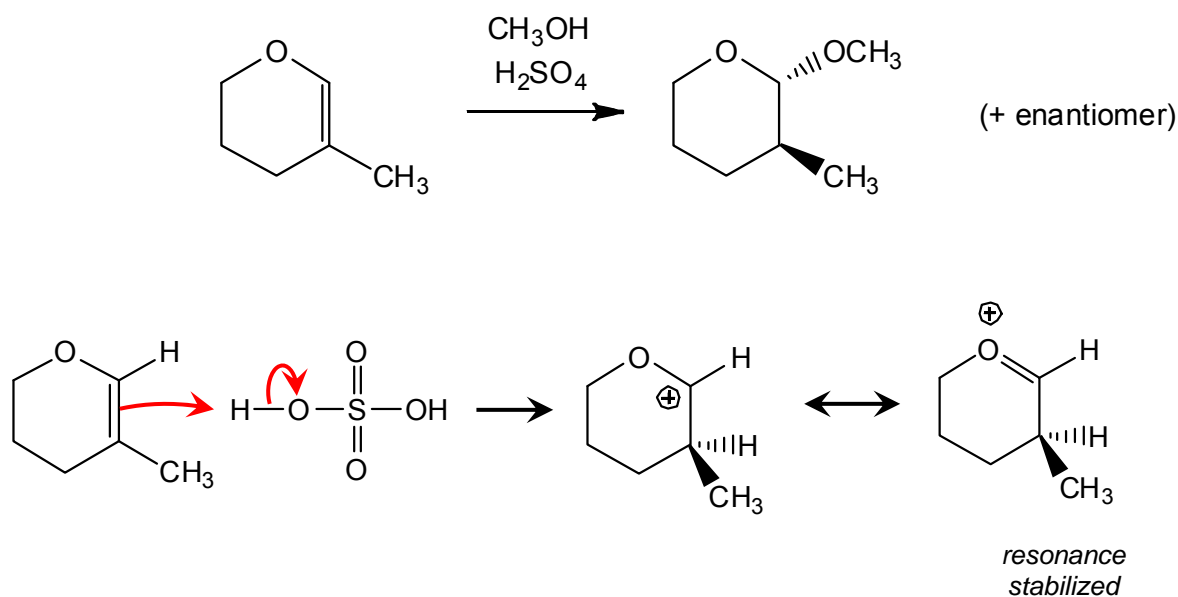


Again, the other enantiomer would come from the bromonium ion forming on the bottom of the alkene instead of the top, and the $-\text{OH}$ then attacking from the top.

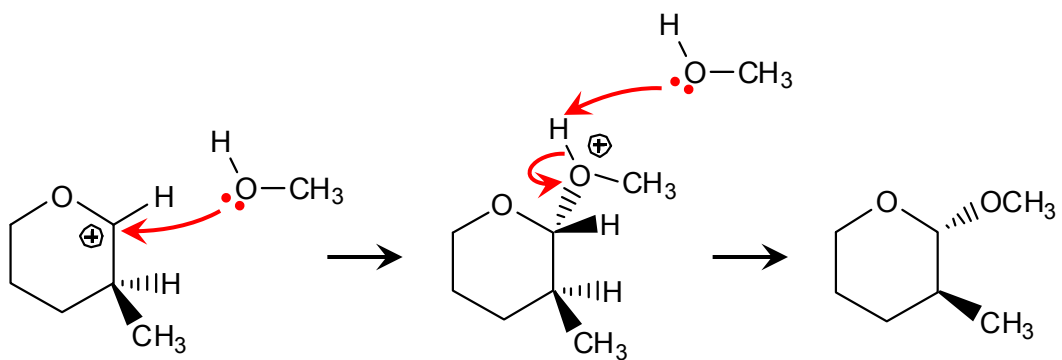




Addition is regioselective and follows Markovnikov's Rule (with the nucleophile attached to the more substituted carbon). This happens because the more stable, tertiary carbocation is preferred.



Here, the preferred carbocation is actually the LESS substituted one. Why? Even though the cation above is a secondary carbocation, it is stabilized by resonance. And resonance is usually more effective at stabilizing cations than substitution.



*methanol approaches
from bottom to avoid
methyl group on top*