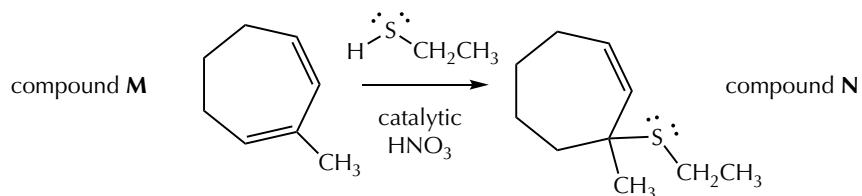
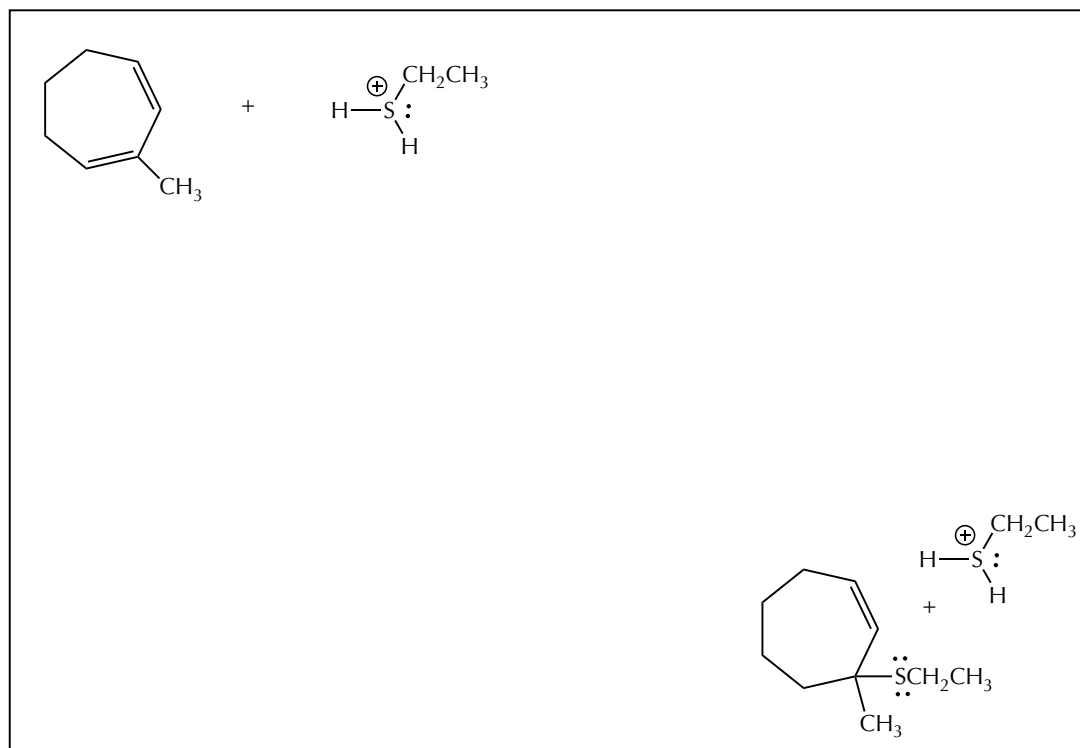


Thinking in Blue #6 is from the book (Q 4.19). This one raises a nice topic (resonance) in electrophilic addition reactions.

- 4.19 Thiols (such as ethanethiol, $\text{CH}_3\text{CH}_2\text{SH}$) participate in many reactions that are analogous to their alcohol counterparts (such as ethanol, $\text{CH}_3\text{CH}_2\text{OH}$). The electrophilic addition reaction of ethanethiol to compound **M** gives compound **N** with a high degree of regioselectivity. Because ethanethiol is a relatively weak acid ($\text{p}K_a = 10.5$), a strong acid catalyst is required.

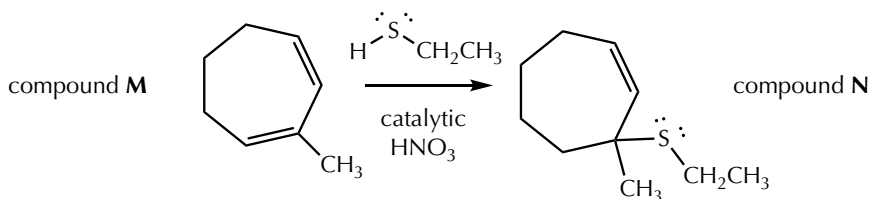


- (a) Provide the complete, stepwise curved arrow mechanism for this reaction (including nonbonding electrons). The most likely acid present in this reaction is the conjugate acid of ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}_2^+$) which, as a true catalyst, is consumed in the first step and reformed in the last step.



- (b) There are four possible protonation sites for the first step, yet the rate of the reaction for the one that gives this product is significantly faster than the other three. Using words and a drawing, provide a complete explanation for why the observed protonation is fastest.
- (c) Which of the other three protonations is the next fastest? Draw it and provide an explanation for your selection.

4.19 Thiols (such as ethanethiol, $\text{CH}_3\text{CH}_2\text{SH}$) participate in many reactions that are analogous to their alcohol counterparts (such as ethanol, $\text{CH}_3\text{CH}_2\text{OH}$). The electrophilic addition reaction of ethanethiol to compound **M** gives compound **N** with a high degree of regioselectivity. Because ethanethiol is a relatively weak acid ($\text{p}K_a = 10.5$), a strong acid catalyst is required.



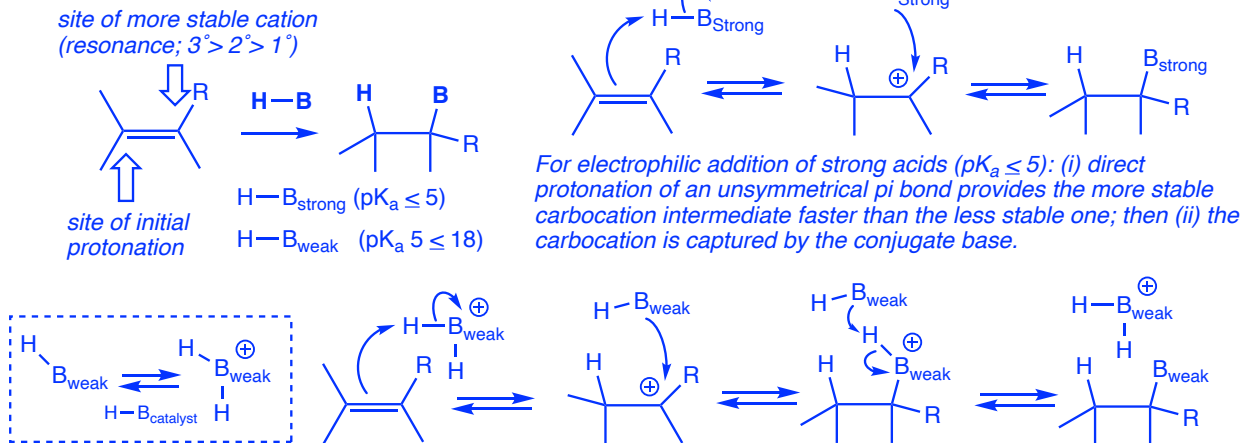
One of the overarching guidelines in the structure for CHEM 210 is to provide the experimental observation for questions where the application of a complete, stepwise mechanism is required for the answer. The idea is to separate out the prediction of outcomes from the story we tell for explaining an outcome. In principle, it makes these types of questions more fair because we never have to face the situation where the prediction of the product is wrong but the proposed mechanism is correct by being consistent with the formation of that incorrect product. So, right away, the full observation is presented here. The unstated corollary is important: **if you happen to think something else ought to be taking place, it does not!**

Although the diagnosis (identification) of the question is quite possible through a reading of the structures, the text of the problem reveals (or reinforces) quite explicitly all of the identification information that is required to classify the question:

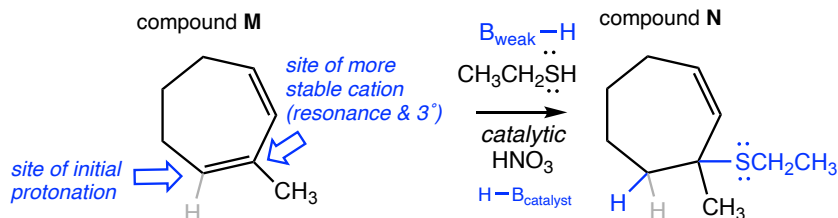
- (1) *electrophilic addition*
- (2) electrophilic addition *of a weak acid (which requires a strong acid catalyst)*
- (3) electrophilic addition of a weak acid (which requires a strong acid catalyst), *in analogy with additions of alcohols*

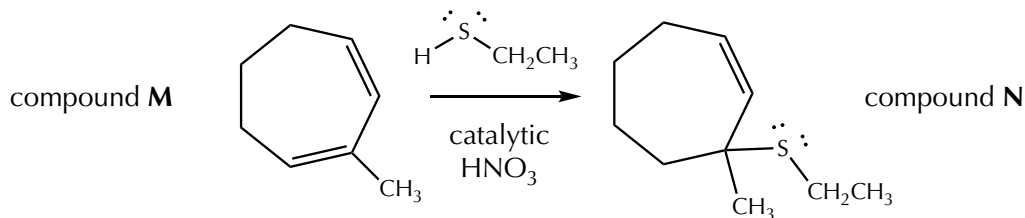
The general concept for an acid-catalyzed electrophilic addition reaction of a weak acid can be applied to thousands of different molecular combinations, once you know you are working with this type of reaction.

electrophilic addition reaction of acids

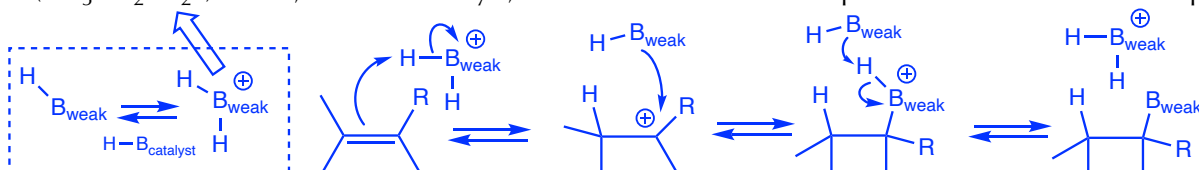


The question is explicit in the identification of the second case (weak acid addition), and so the various components of the reaction can also be identified from among the structures presented.



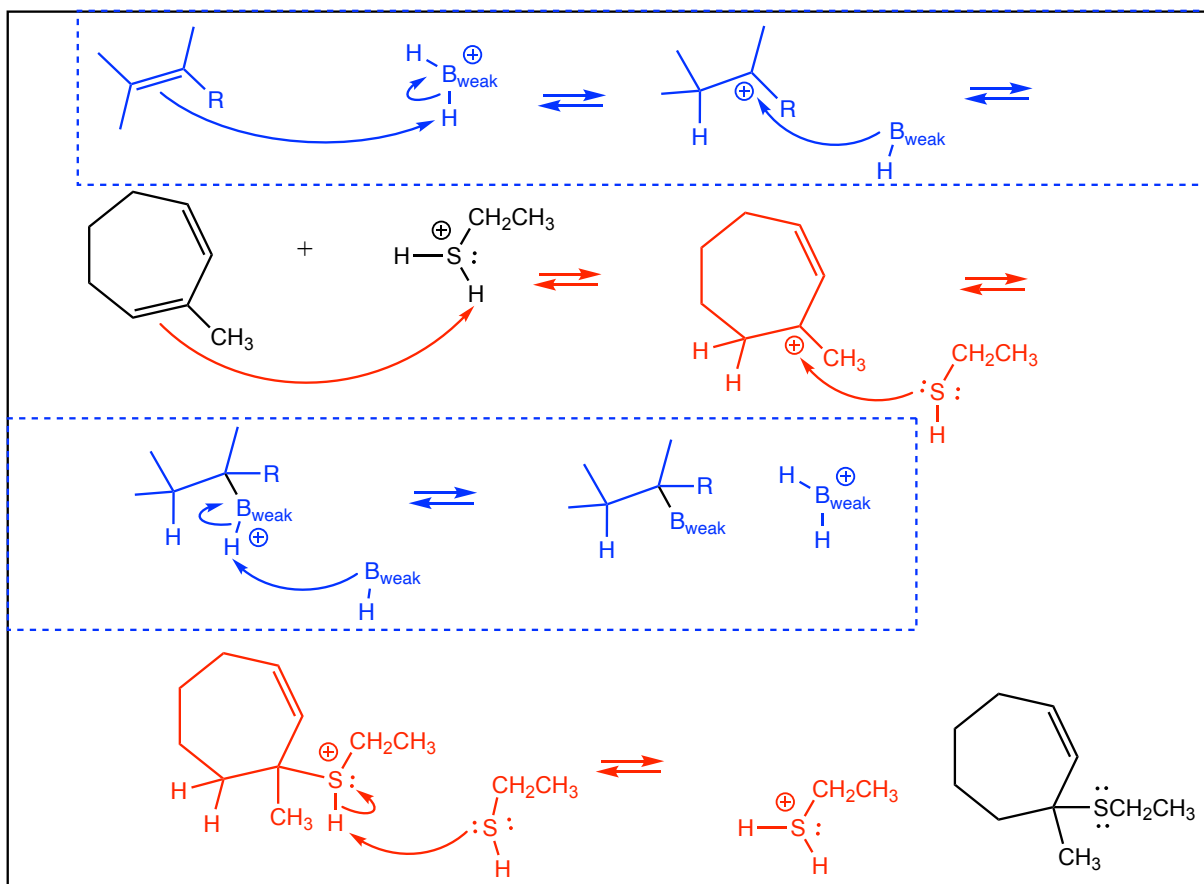


- (a) Provide the complete, stepwise curved arrow mechanism for this reaction (including nonbonding electrons). The most likely acid present in this reaction is the conjugate acid of ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}_2^+$) which, as a true catalyst, is consumed in the first step and reformed in the last step.

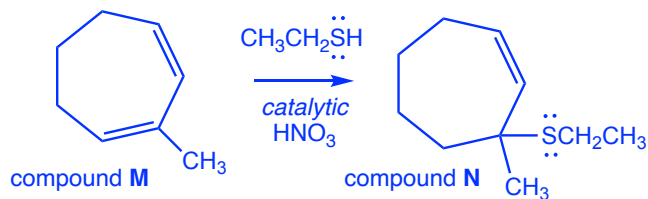
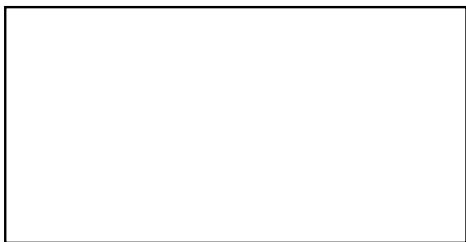


For electrophilic addition of weak acids ($pK_a \leq 18$), the conjugate acid of the weak acid needs to be formed using a strong acid catalyst, then: (i) direct protonation of an unsymmetrical pi bond provides the more stable carbocation intermediate faster than the less stable one; (ii) the carbocation is captured by the original weak acid; (iii) the resulting cationic intermediate needs to be deprotonated to provide the addition reaction product.

The text for part (a) reaffirms the weak acid conditions by talking about the need to have the conjugate acid of the original weak acid as the true catalyst for the reaction. The statement also speaks directly to the first and last steps of the mechanism, where the catalyst is consumed (reacted) in the first step and then reformed in the last step.



- (b) There are four possible protonation sites for the first step, yet the rate of the reaction for the one that gives this product is significantly faster than the other three. Using words and a drawing, provide a complete explanation for why the observed protonation is fastest.

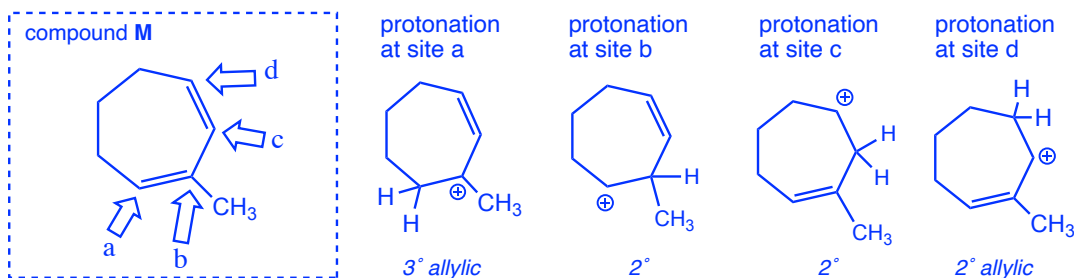


The text of the question says:

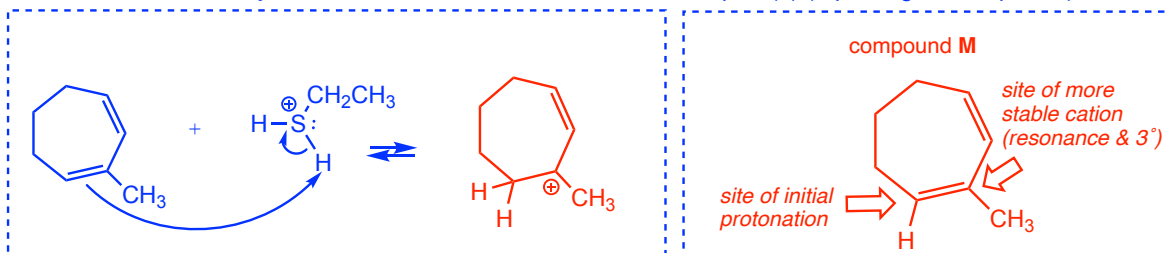
- A. there are many carbocation options (four sites for protonation)
 B. three of the options are not as good as the one observed

At this point, you need to explore different carbocation options AND keep in mind the factors that provide stability [resonance, followed by degree of substitution: $3^\circ > 2^\circ > 1^\circ$].

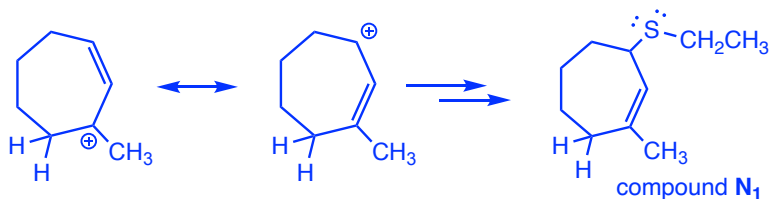
The "four sites" for protonation are the other four sp^2 atoms of the starting material, compound **M**.



There are two ideas here: (1) protonation gives a carbocation and (2) that the more stable carbocation is formed faster [stability derived from resonance, followed by degree of substitution: $3^\circ > 2^\circ > 1^\circ$]. These reminders should reinforce the reason why this was the addition reaction selected for part (a) (repeating that step here):



A last note for completeness: the delocalization of the cation that gives compound **N** can also potentially give compound **N₁** and this is a different question than the one posed here.



- (c) Which of the other three protonations is the next fastest? Draw it and provide an explanation for your selection.

Already done! What a surprise. The 2° allylic (protonation at site d, as shown above) is the only other resonance-stabilized cation, so it forms next fastest.

