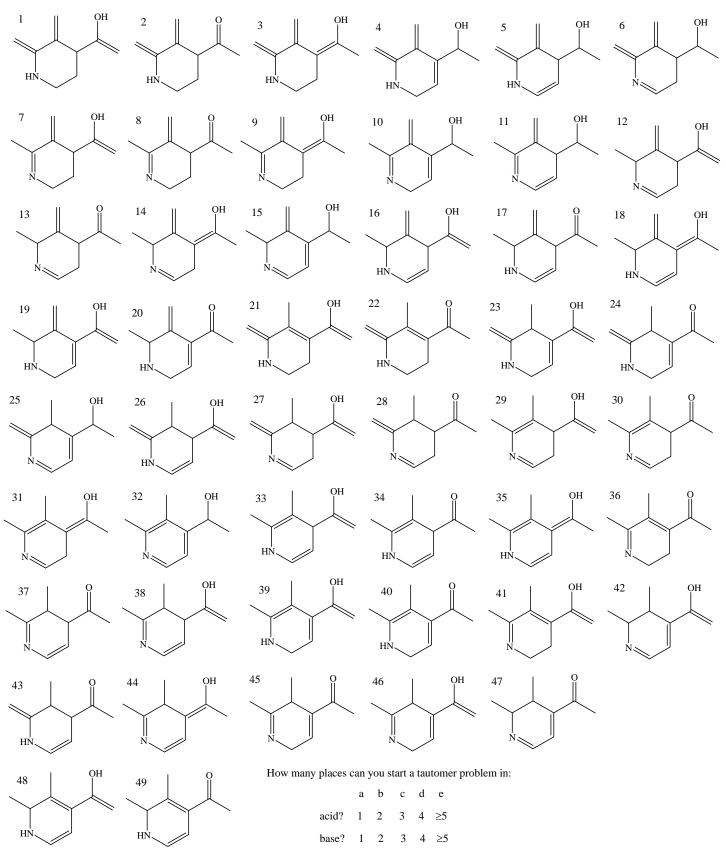
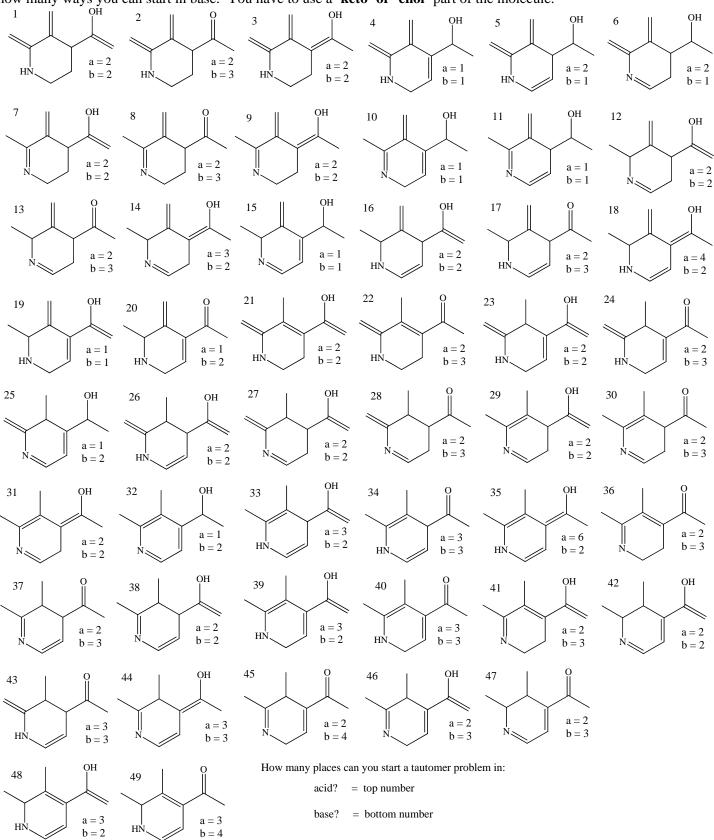
Possible tautomer problems (49 x 48 = 2352 possibilities in acid or base x 2 = 4704 problems). There could be some duplicates and there could be some missing possibilities. My eyes were going buggy, so I had to give up.

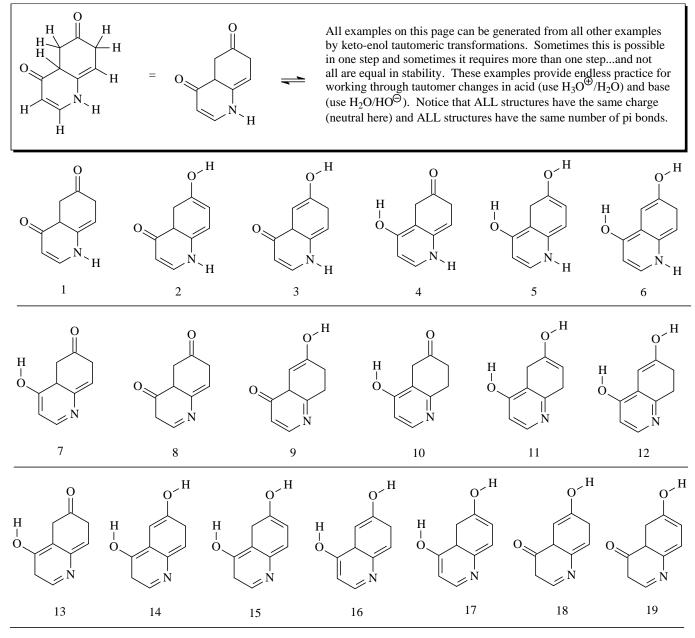


2

The top number shows how many ways you can start a tautomer problem in acid and the bottom number shows how many ways you can start in base. You have to use a **'keto' or 'enol'** part of the molecule.



## More Examples of Tautomer Problems



Almost certainly there are more tautomers, but this is all my brain could think of at the moment. Remember the general strategy for each tautomeric transformation:

1. proton transfer

- 2. resonance delocalized intermediates
- 3. proton transfer

<u>In acid</u>

- 1. proton on (from  $H_3O^{\textcircled{}}$ )
- 2. resonance

3. proton off (with  $H_2O$ )

In base

- 1. proton off (with  $HO^{\ominus}$ )
- 2. resonance
- 3. proton on (with  $H_2O$ )

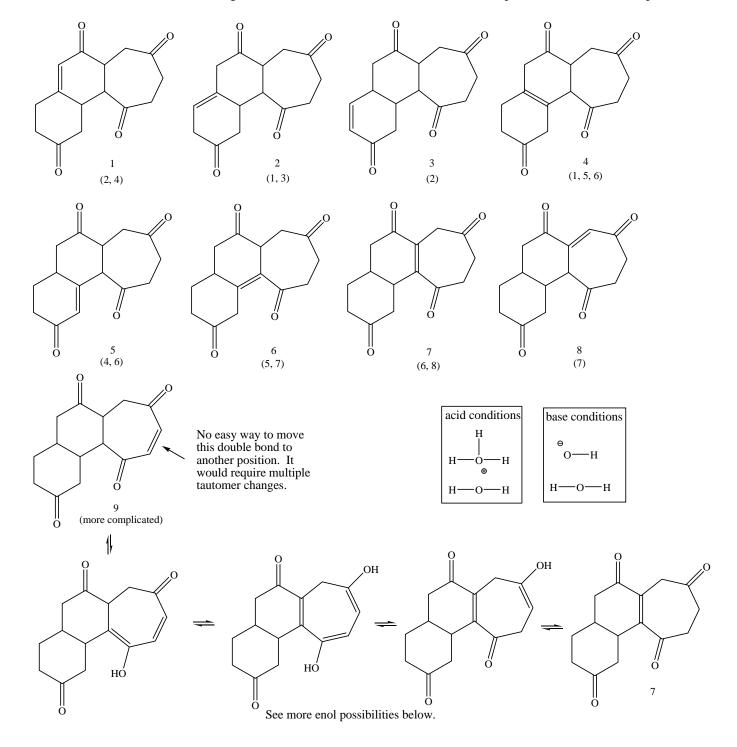
Note – There is the same number of pi bonds and same total charge in each tautomer. Every tautomer can be mechanistically converted into every other tautomer  $(1 \rightarrow 2 \text{ is a different problem than } 2 \rightarrow 1)$ . These interconversions can be done in acid or in base, which means there are  $(18 \times 18 \times 2) = 648$  problems just on this page. This isn't the kind of topic you can memorize. You need to develop a systematic approach and practice your strategy until it becomes a workable tool for you.

## Chem 315/316 Keto-Enol Tautomer Handout

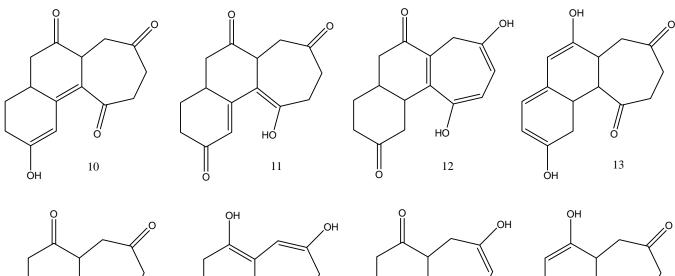
## Beauchamp

4

Problem – The C=C pi bond can be moved around to all possible positions. Show how this might be done in acid and base conditions. You will have to use "enols" (in acid) or "enolates" (in base) to help in these transformations. Consider how many C-H positions are enolizable. The answers may surprise you. Only "keto" tautomer forms are shown below. There are many, many "enol" variations of those "keto" forms (see some of these on the next page). The number in parentheses shows other "keto" tautomers that can be made in a single keto/enol tautomer change (connected by resonance). For example, tautomer 1 can make (or be made from) tautomers 2 and 4 in a single tautomer change. Other changes, for example 1 to 3, would require more tautomer cycles. Notice that every tautomer below has the same charge (neutral here) and the same number of total pi bonds (5 in this example).



Here are a few additional helpful "enol" tautomers connecting one "keto/enol" system to another "keto/enol" system. There should be four "keto/enol" systems in this problem, plus one extra C=C pi bond in conjugation with one or more of them. If a tautomer below does not have that, it is wrong.



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