

# Chapter 13 Practice Problems

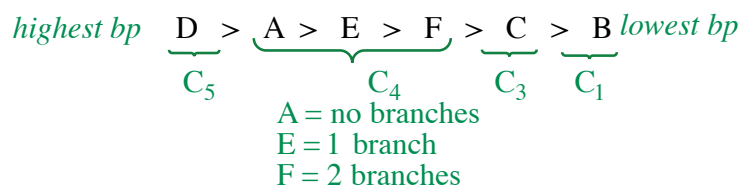
## *Solutions*

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- A 1-bromo-4-heptanol      B 7-bromo-3-heptanol  
C 3,3-dimethylcyclopentanol      D 3,5-dimethyl-3-hexanol
- 

- all of these compounds are alcohols, so all are polar and hydrogen bonding
- they differ in molecular weight (remember: higher molecular weight translates into higher boiling points)
- they also differ in branching (branching decreases boiling point relative to lesser branched or straight chain isomers)

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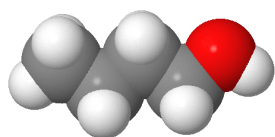


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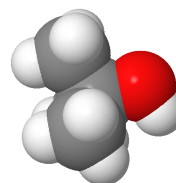
A. methanol, ethanol and the propanols are all polar hydrogen bonding alcohols with relatively small R groups. Thus, the OH group dictates their solubility in water via hydrogen bonding despite the presence of the small hydrophobic methyl, ethyl and propyl groups.

B. The n-butyl R group on n-butanol is sufficiently large that its nonpolar, non-hydrogen bonding hydrophobic character keeps it from dissolving in the very polar hydrogen bonding water.

C. Since R groups relay their intermolecular forces over their entire surface area, the n-butyl group is much more hydrophobic than the *tert*-butyl group because of the much lower surface area of the ball-like *tert*-butyl group (remember, the least surface area for a given volume is that of a sphere). Therefore, the OH group of *tert*-butanol is sufficient to engage in hydrogen bonding with the water to allow for solubility despite the presence of a hydrophobic R group (similar to methanol, ethanol and the propanols). The space filling models (from ChemMagic) are provided below:



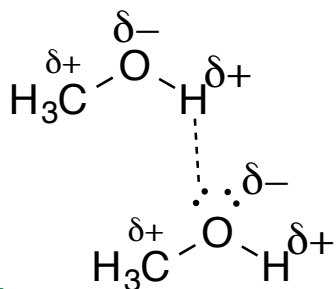
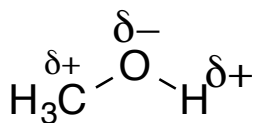
n-butanol  
(hydrophobic R group occupies lots of space)



*tert*-butanol  
(hydrophobic R group much more compact due to branching)

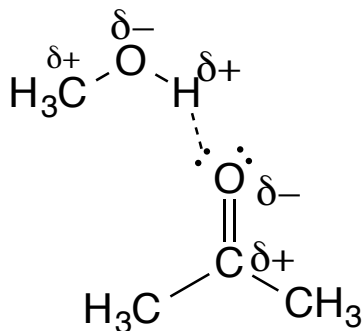
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- the electronegative O polarizes electrons onto itself relative to the less electronegative C and the H to which it is attached, giving it a  $\delta^-$
- the  $\delta^+$  on H is greater than that on C because H has less electron density to donate to the O than does the C



- the  $\delta^+$  on the H atom is strongly attracted to the  $\delta^-$  on the O of a neighboring molecule electrostatically as it tries to find additional electron density
- this strong electrostatic attraction is termed a hydrogen bond

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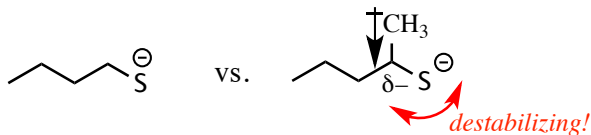


- as in the hydrogen bond between two methanol molecules, the  $\delta^+$  on the H of a methanol molecule is attracted to the lone pair of a neighboring O atom (with a  $\delta^-$  from the polar bond to the carbon to which it is attached)
- in this case, the methanol molecule is considered to be the hydrogen bond donor and the acetone molecule is the hydrogen bond acceptor

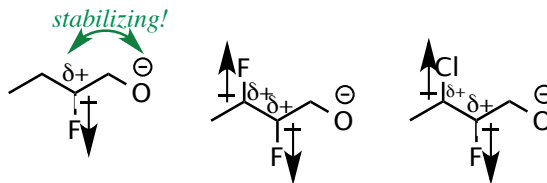
- The first obvious difference between these molecules is that some have SH bonds and others have OH bonds (they all have CH bonds but those are typically not acidic hydrogen atoms)
- according to the ARI priorities, the SH containing compounds D and A will be more acidic than the OH containing compounds because the negative charge of the conjugate base is more stable on the larger S atom than the smaller O atom (Atom effect)



- between A and D, D will be more acidic than A because the methyl group on A acts as an electron-donating group which will decrease the stability of the conjugate base (Inductive effect)



- likewise, E will be less acidic than G for the same reason
- B, C and F will be more acidic than G because they contain electron-withdrawing groups that help stabilize the negative charge of the conjugate base. In particular, each has a F not distant from the negatively charged O that stabilizes the charge because of the  $\delta^+$  created by the polar bond to C.



- compounds C and F have TWO carbon-halogen bonds versus the one carbon-halogen bond in B. The second polarized bond will further stabilize the negatively charged O. So compounds C and F will be more acidic than B. Note that these bonds will not stabilize the negatively charged O as strongly as the first C-F bond because they are further from the negative charge. Nevertheless, they offer some additional (albeit weaker) stabilization.
- Since the C-F bond is more polar than the C-Cl bond (greater difference in electronegativity in the C-F bond), the  $\delta^+$  created by that bond is larger than that on the C-Cl bond, and is therefore more stabilizing
- putting all of this together, we can rank the acidities as:

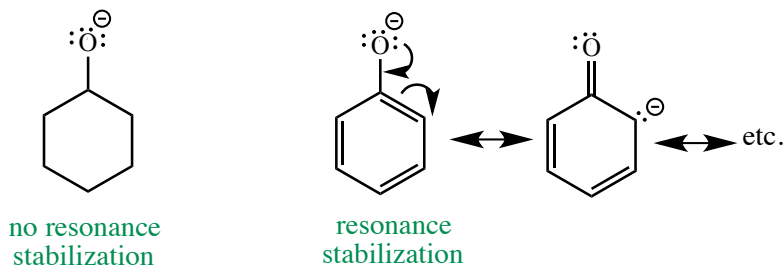
*most acidic* D > A > C > F > B > G > E *least acidic*

- The first obvious difference between these molecules is that some have NH bonds and others have OH bonds (they all have CH bonds but those are typically not acidic hydrogen atoms)
- according to the ARI priorities, the OH containing compounds B, C and D will be more acidic than the NH containing compound A because the negative charge of the conjugate base is more stable on the more electronegative O atom than the less electronegative N atom (Atom effect)

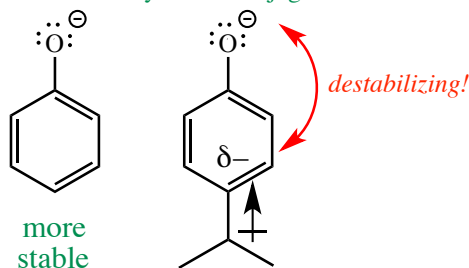


- C and D have OH groups attached to unsaturated benzene rings whereas B has an OH group attached to a saturated cyclohexane ring. The negatively charged conjugate bases of C and D will therefore be more stable than that from B because they can engage in resonance stabilization while the conjugate base from B cannot. Therefore C and D will be more acidic than B.

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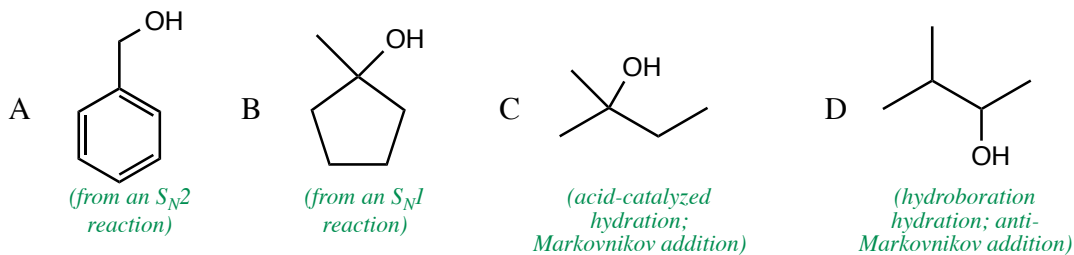


- compound D has an isopropyl group attached to the ring which acts as an electron donating R group. The presence of an electron donating group will decrease the stability of the conjugate base and lower the acidity

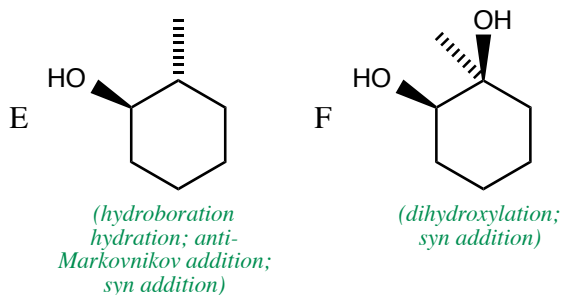


- putting all of this together, we can rank the acidities as:

*most acidic* C > D > B > A *least acidic*

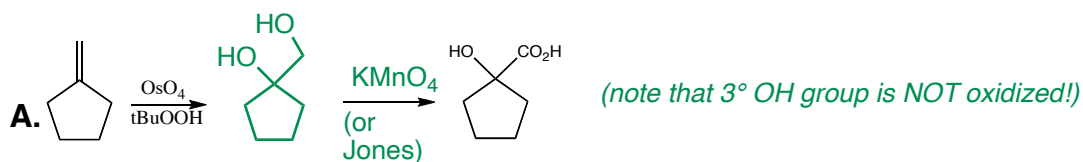
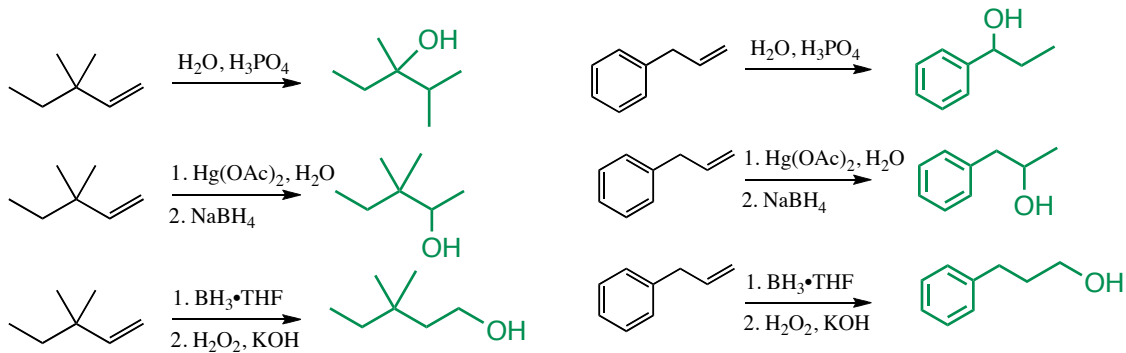


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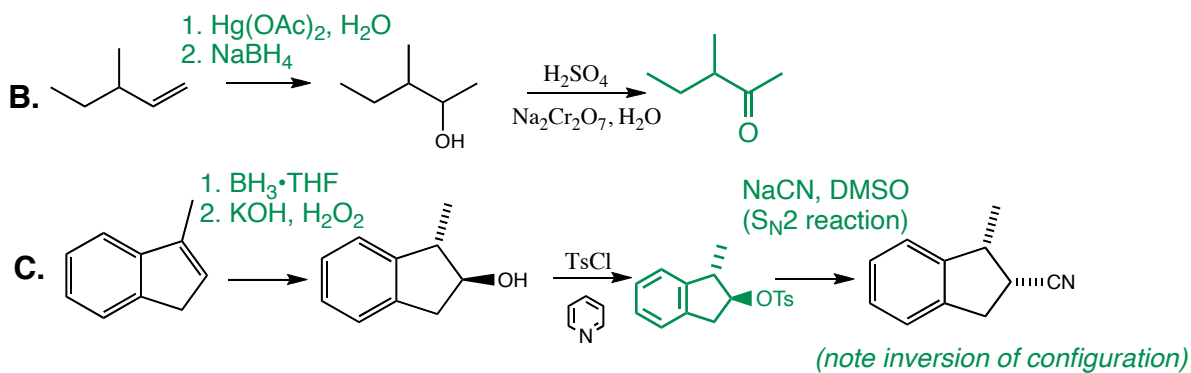


- remember: we can only verify syn and anti addition when dealing with cyclic substrates!

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