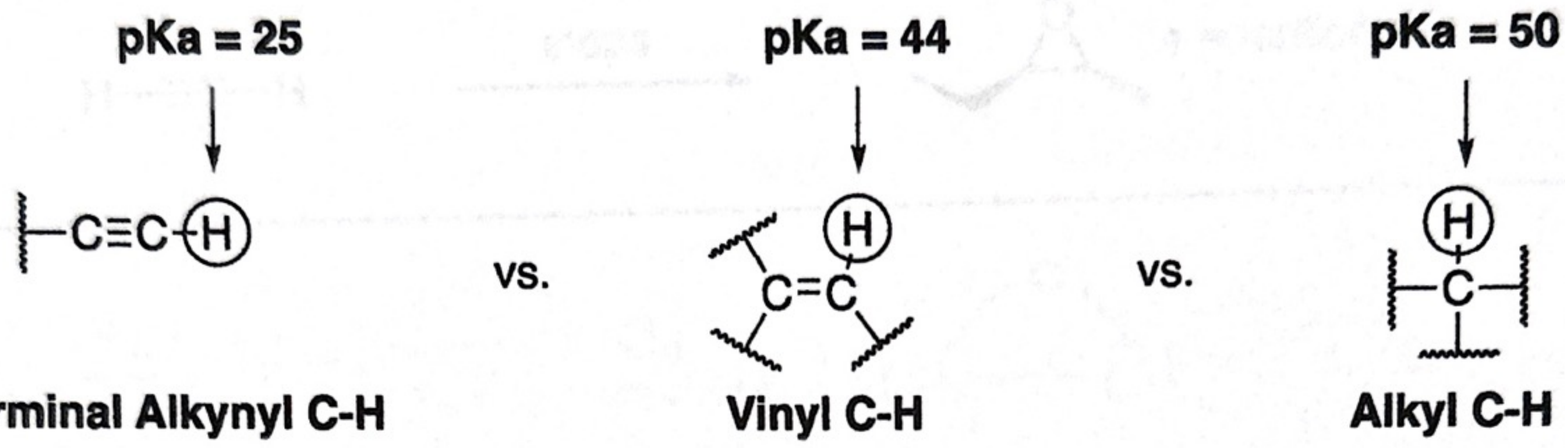
Your Name:

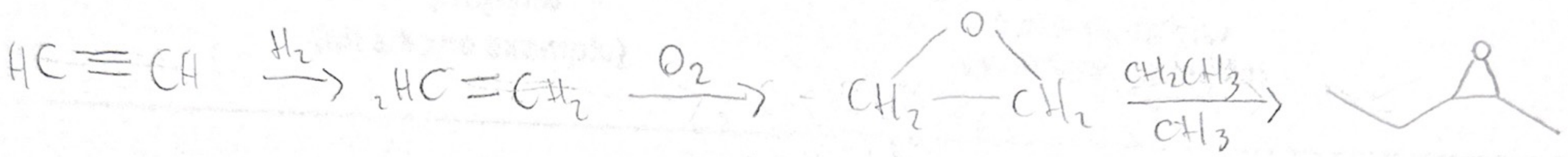
Alkynes have a very interesting structure as they consist of a sigma bond and two separate pi-bonds to make up the overall triple bond characteristic of the alkyne functionality.

1. Consider the structures below and discuss the reason for the different pKa values being indicated for the C-H bond of a terminal alkyne vs. vinyl C-H (alkene) vs. alkyl C-H bond. From these values it is clear that the terminal alkyne is most acidic (lower pKa). Your discussion needs to address the reason why rather than simply say "because the pKa is lower". Why is the pKa lower?

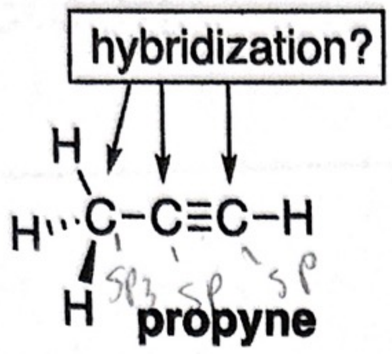


Because alkynes are sp-hybridized & alkenes are sp_2 & alkanes are sp_3. sp is the most electronegative & acidity increases with electronegativity.

2. Terminal alkynes are a valuable carbon source due to their relatively more acidic C-H bond. Furthermore, the C-C triple bond of an alkyne can be further reacted upon to form other useful functional groups. Consider the transformation below and propose a synthesis for the product being indicated starting from the acetylene (otherwise known as ethyne). You may use any other reactions that have been covered in chapter 9 as well as those covered in previous chapters of the text. Show all reagents needed and draw the product expected after each step in your proposed synthesis. It may be helpful to draw out a retrosynthetic scheme first so that you have a workable plan for your synthesis. Make sure that the reactions used are consistent with the relative stereochemistry indicated in the product shown.

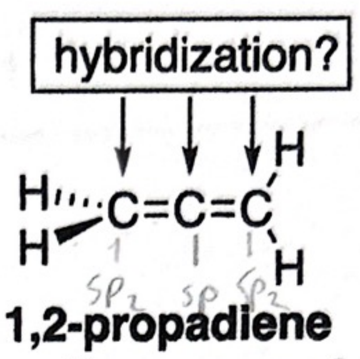


3. Allenes have both similar and different structural properties compared to alkynes. Look up the three-dimensional orbital diagram for both an alkyne and an allene. Then, redraw each structure below showing the hybrid atomic orbitals clearly. Label the specific hybrid orbitals that overlap to make the sigma-bonds and also label each of the p-orbitals clearly. It will be helpful to first know what the hybridization of each carbon atom is when doing this so that you know what atomic orbitals (hybridized and unhybridized) are available to hold the bonding and non-bonding electrons. In your drawing, be sure to clearly illustrate the plane each of the pi-bonds are oriented about and explain why different planes are required for each of the pi-bonds, respectively.



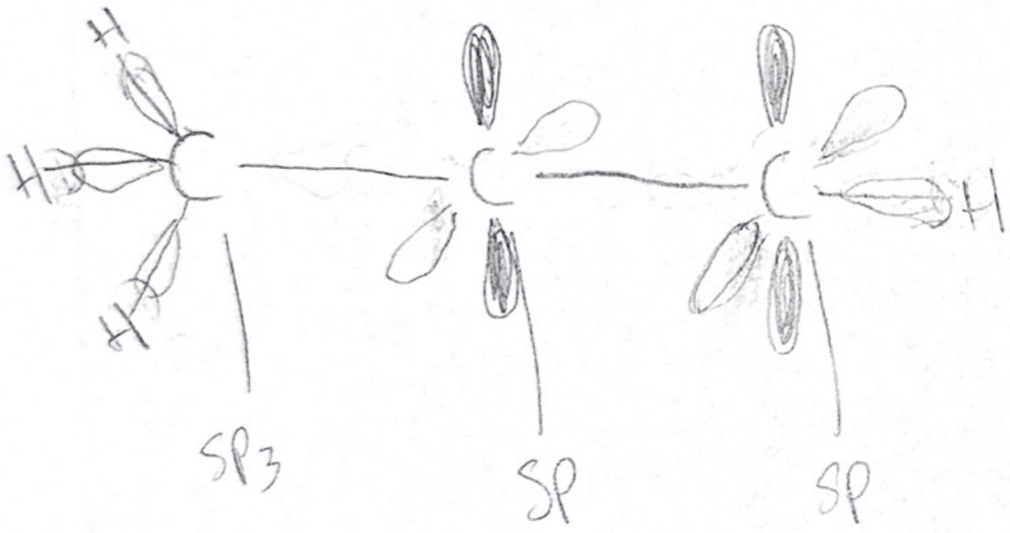
propyne
(an alkyne example)

vs

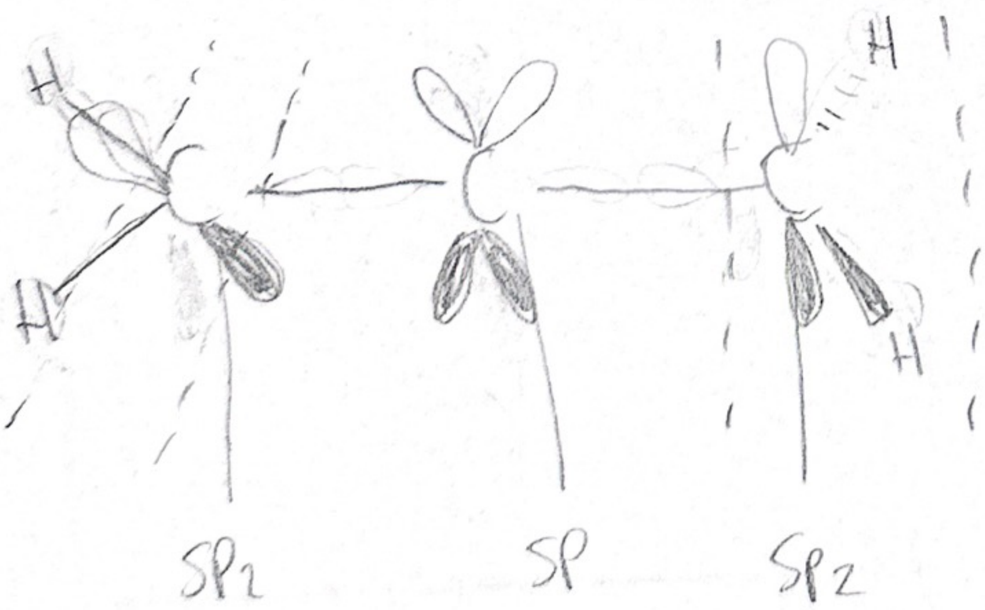


1,2-propadiene
(an allene example)

Propyne



1,2-propadiene

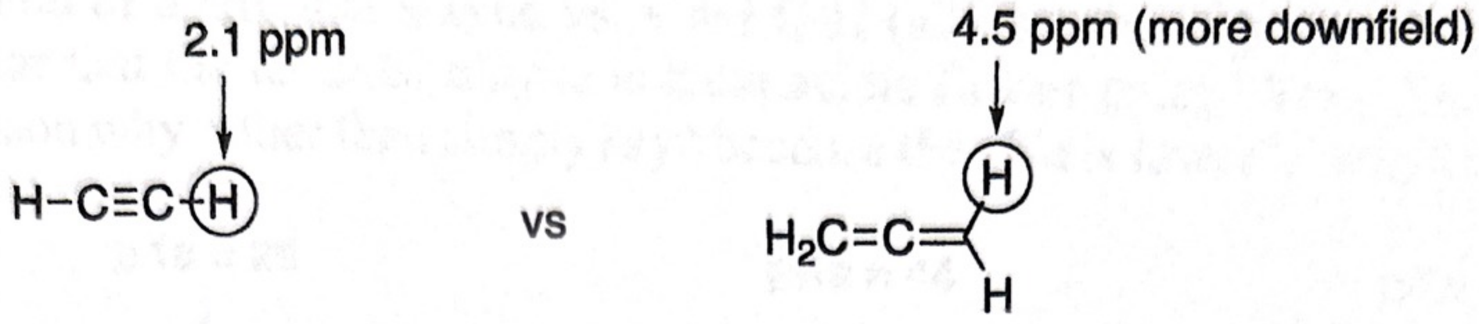


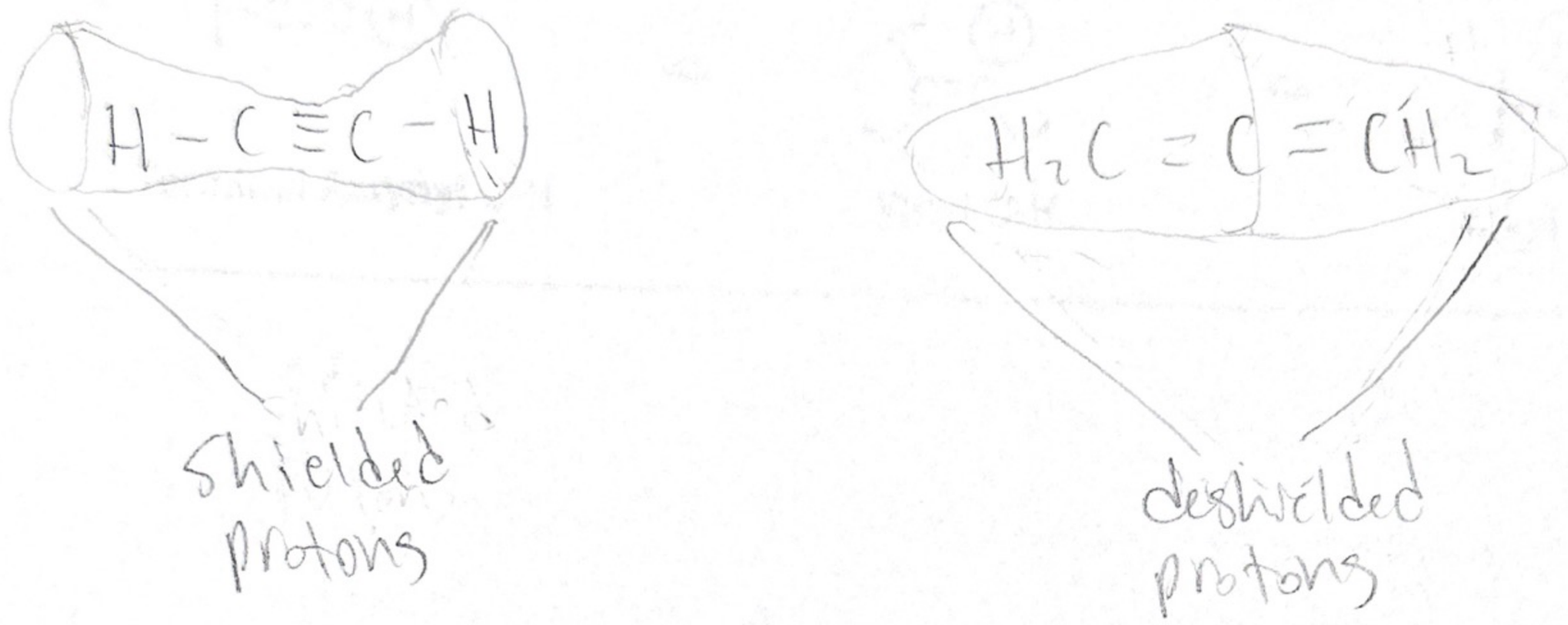
atoms of pi bonds are on the same plane because they cannot rotate around a pi bond.

– perpendicular pi bond

– perpendicular pi bonds & methyl groups

4. Interestingly, although the alkyne and allene look similar in terms of the orbitals, the protons attached to them have very different 1H NMR chemical shifts. The allene proton chemical shift is approximately 4.5 ppm whereas the alkyne proton chemical shift is approximately 2.1 ppm. Propose a reason for why these two protons have drastically different 1H NMR chemical shifts. (Hint: look up the concept of ring currents). Draw a picture that illustrates this explanation clearly.





Shielding causes a lower frequency by protecting the protons from chemical shifts. Nuclei with more electron density are more shielded.