

Chemistry 125 1998 answers

2. b) **UNDERLINE** the approximate frequency for a C-H bond stretching vibration.

IR frequencies are in the range 10^{13} to 10^{14} Hz, C-H stretching is near the high frequency end of the range because of the small mass of H. The answer is 10^{14} Hz.

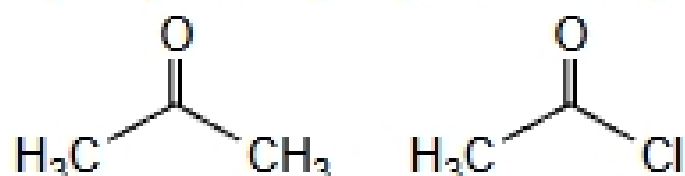
3. (4 minutes) A tiny amount of acid (say one part in 10^5) can change the NMR spectrum of CH_3OH dramatically, while it has no noticeable effect on the IR spectrum of the same alcohol. Explain this difference.

For an OH group, both the chemical shift in NMR and the vibration frequency in IR would depend on the amount of H-bonding. For any given OH group, the H-bonded pattern is changing so rapidly on the slow NMR time scale (perhaps 1/1000 second, corresponding to 10 ppm at 100 MHz for the range of chemical shifts of the different patterns) that the NMR chemical shift is averaged to a single value (see text Figure 13.44 for EtOH); but it is changing so slowly on the rapid IR time scale (perhaps 10^{-13} second from the range in vibration frequencies) that one sees a separate peak for non-H-bonded OH and a broad envelope of many different kinds of H-bonded peaks. (See text, Figure 17.14)

Such a tiny amount of acid would not appreciably change the relative numbers of various potential H-bonded patterns in a methanol solution. The number of protonated CH_3OH molecules would be far too few to see directly with either technique, so one might at first expect no effect.

However, the small concentration of acid is enough to catalyze proton exchange among the methanol molecules and make it fast on the NMR time scale. Thus not only does a given OH proton see many different H-bonded environments (as above, where it remained attached to a single molecule) but as it moves from molecule to molecule it sees the average field due to magnetism of many different sets of methyl protons on different CH_3O frameworks. So in NMR the spin-spin splitting disappears with a tiny amount of acid (compare figure 13.44 and 13.45 one p. 362 of text). The exchange is too slow to influence the IR (obviously protons should not shift from molecule to molecule anything like as fast as they vibrate against the atom to which they are bonded, which is what IR is looking at).

4. (4 minutes) How would you use IR spectra to distinguish most easily between the following compounds? Say as specifically as possible what you would expect to see.



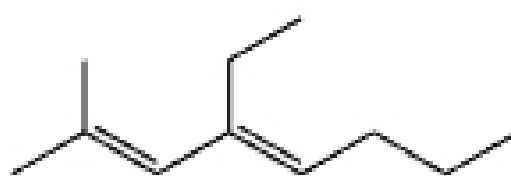
One would look at the strong (i.e. intense or tall) C=O stretching peak. In the ketone it would come at about $1715/\text{cm}$, in the acid chloride at about $1800/\text{cm}$. (The reason for the higher frequency in the acid chloride is that the C=O bond is strengthened due to overlap of an unshared pair of electrons on the oxygen with the σ^* C-Cl orbital.)

[A common error was to confuse strength of the *absorption* (due to polarity of the bond) with strength of the *bond*, which influences the *frequency*, not the intensity or strength, of the absorption. i.e. bond strength influences the x axis of the IR spectrum; bond polarity, the y axis.]

5. (4 minutes) Insert appropriate reagent(s) above each of the following arrows.

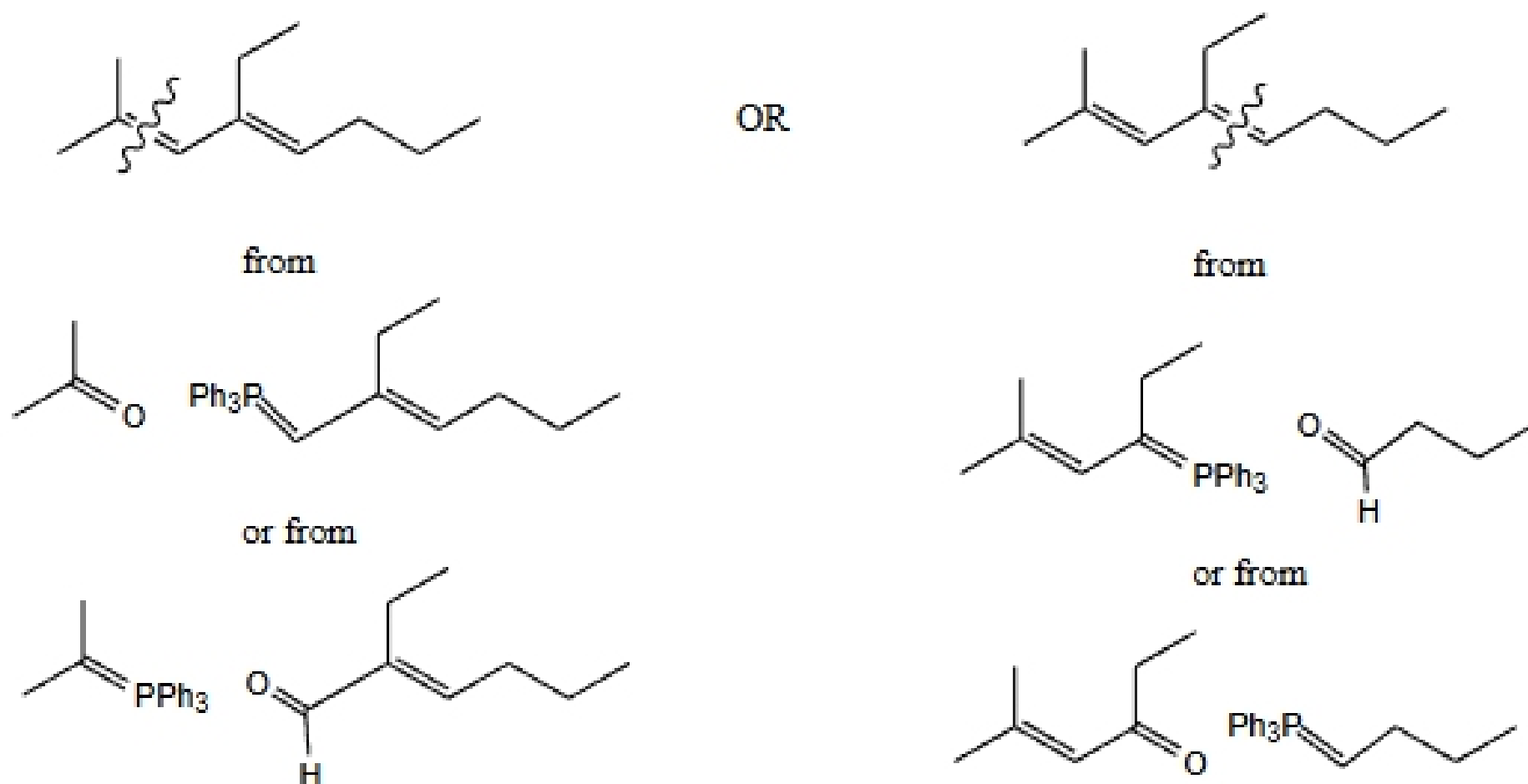


6. (8 minutes) Suggest a high-yield synthesis of the following compound from materials with four or fewer carbons. (Do not worry about E/Z isomers)



[This was one of the assigned problems from Chapter 16, number 6d, see answer book]

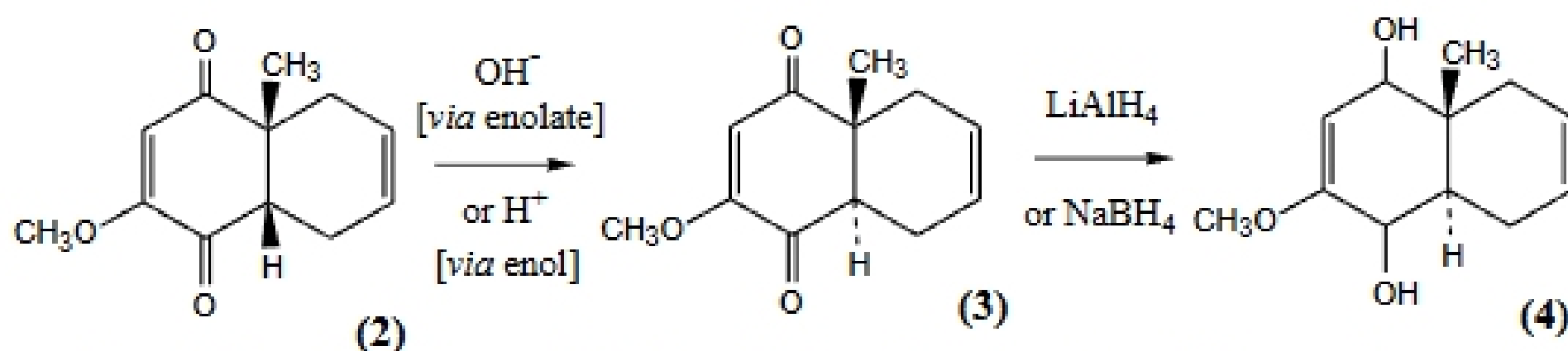
One of the best ways to assemble C=C double bonds in a controlled way (avoiding the mixtures of isomers that result from elimination reactions) is the Wittig reaction. One could consider either of the two double bonds as a candidate for formation by the Wittig procedure:



The bottom row involves α,β -unsaturated carbonyls (aldol products!), and the bottom left example starts with the product from aldol condensation of butanal with itself, avoiding the problems of mixed aldol reactions. Thus only two reactions are required: base catalyzed reaction of butanal with itself and reaction of the product with the Wittig reagent from treating 2-trimethylphosphoniumpropane with a strong base such as phenyllithium.

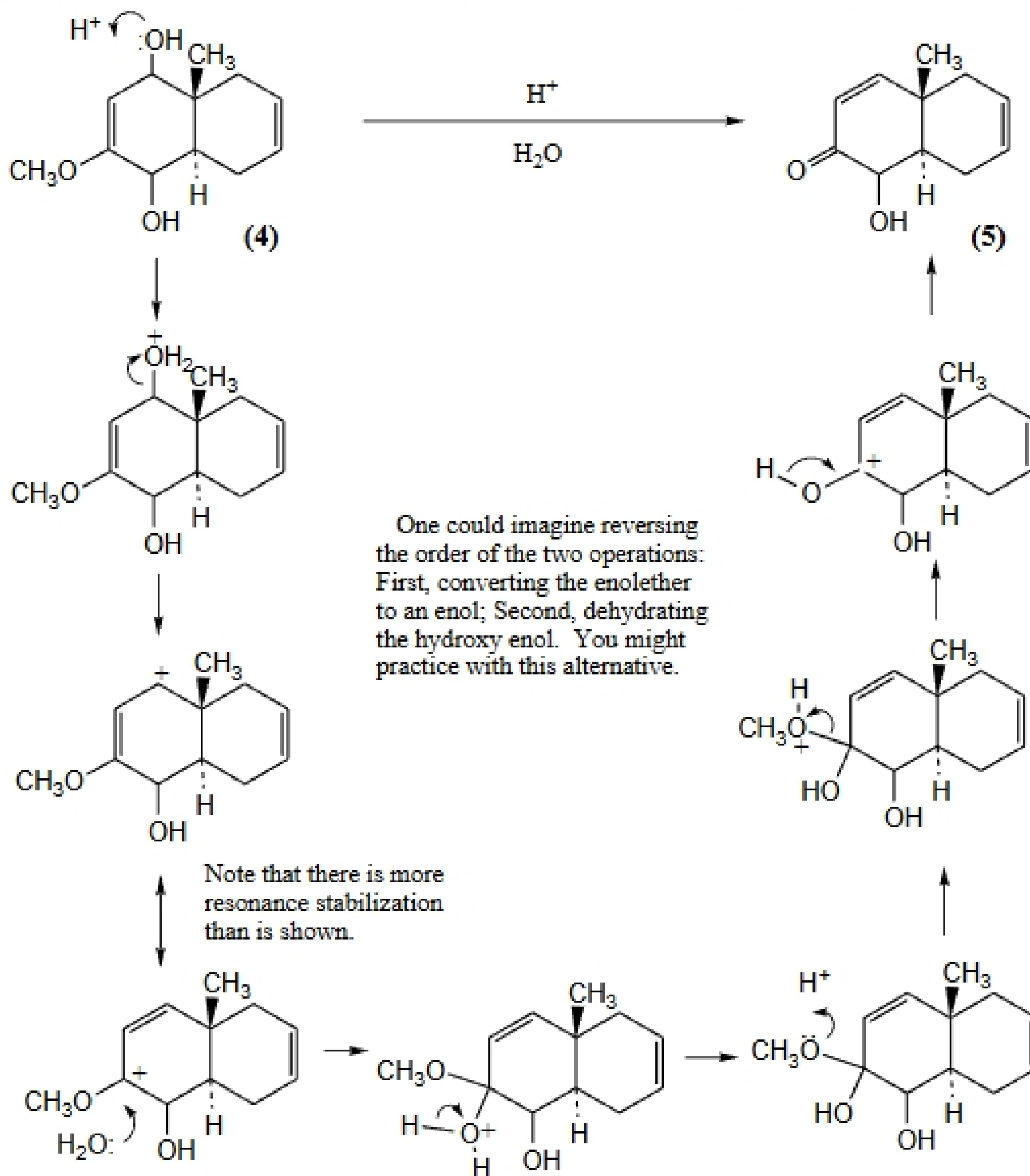
7. (4 minutes) Early in his Cortisone synthesis Woodward converted Compound 2 into Compound 4 by successive treatment with two reagents. Complete the structure of Compound 3, and draw the appropriate reagent above each arrow. (Note the stereochemistry. No mechanisms necessary)

[Some answers overlooked the necessity of completing structure 3]



[Note that the order of the steps is important. After reduction there is no forming an enolate or enol]

8. (10 minutes) Woodward next prepared α,β -unsaturated ketone **5** by treating **4** with acid and water. Complete the partial structures below with necessary atoms, bonds, and arrows (curved, straight, double-headed) to show every bonding change involved in this conversion. Draw only ONE curved arrow in each structure. You may wish to use some structures to show resonance.



9. (4 min) Draw the structure of a compound *with just one ring* that might give Compound **5** upon treatment with base. (You need not draw the mechanism, just the structure of the precursor.)

The α,β -unsaturated ketone screams out "ALDOL"