

(NMR chemical shifts are given on the last page.)

1. (3) In NMR, a radio-frequency photon is absorbed and a peak registers for a proton when the condition of resonance is achieved for that proton. What requirements must be met in order for this to happen?

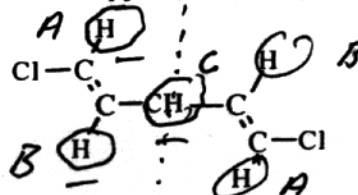
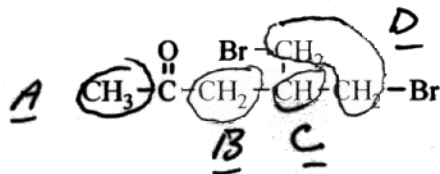
The E_{photon} must equal the ΔE between the +1/2 and -1/2 spin states, created by the magnetic field.

2. a) (4) The diagnostic region of an infrared spectrum covers the range from about 4000 to 1500 wavenumbers. The units for wavenumber are cm⁻¹.

b) (2) Absorption of infrared radiation by a particular bond can occur when the infrared photon energy equals

the ΔE between the vibrational energy levels.

3. (12) For each compound below, circle and label (A, B, C, etc.) the sets of protons that would be responsible for the main peaks in its NMR spectrum. For each main peak, indicate the approximate chemical shift, the relative peak area, and the multiplicity. Use standard abbreviations; for example, δ = 2.3 ppm (2H, d of t).



Peak δ (ppm)

δ (ppm)

A 2.3 ppm (3H, s)

7 ppm (1H, d)

B 2.7 ppm (2H, d)

5 ppm (1H, d of t)

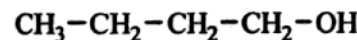
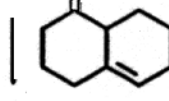
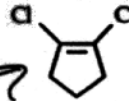
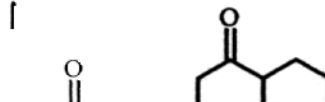
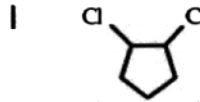
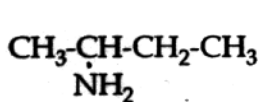
etc.

C 6.8 ppm (1H, t of quin)

2.5 ppm (1H, t)

D 3.5 ppm (4H, d)

4. (8) Four pairs of compounds are shown below. For each pair, indicate whether or not the two members of the pair can be readily distinguished by a casual inspection of the diagnostic regions of their IR spectra.



yes ___ no X

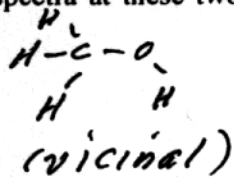
yes ___ no X

yes ___ no X

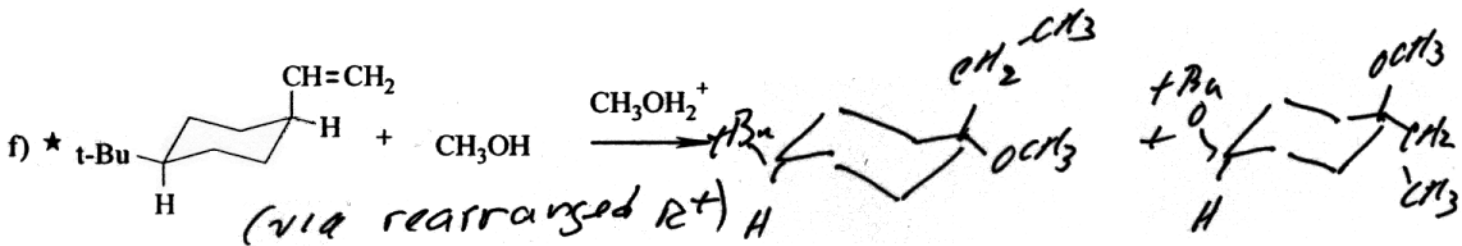
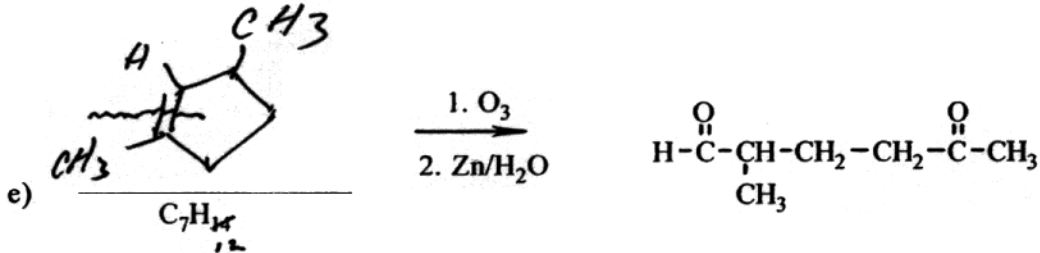
yes ___ no X

symmetrical

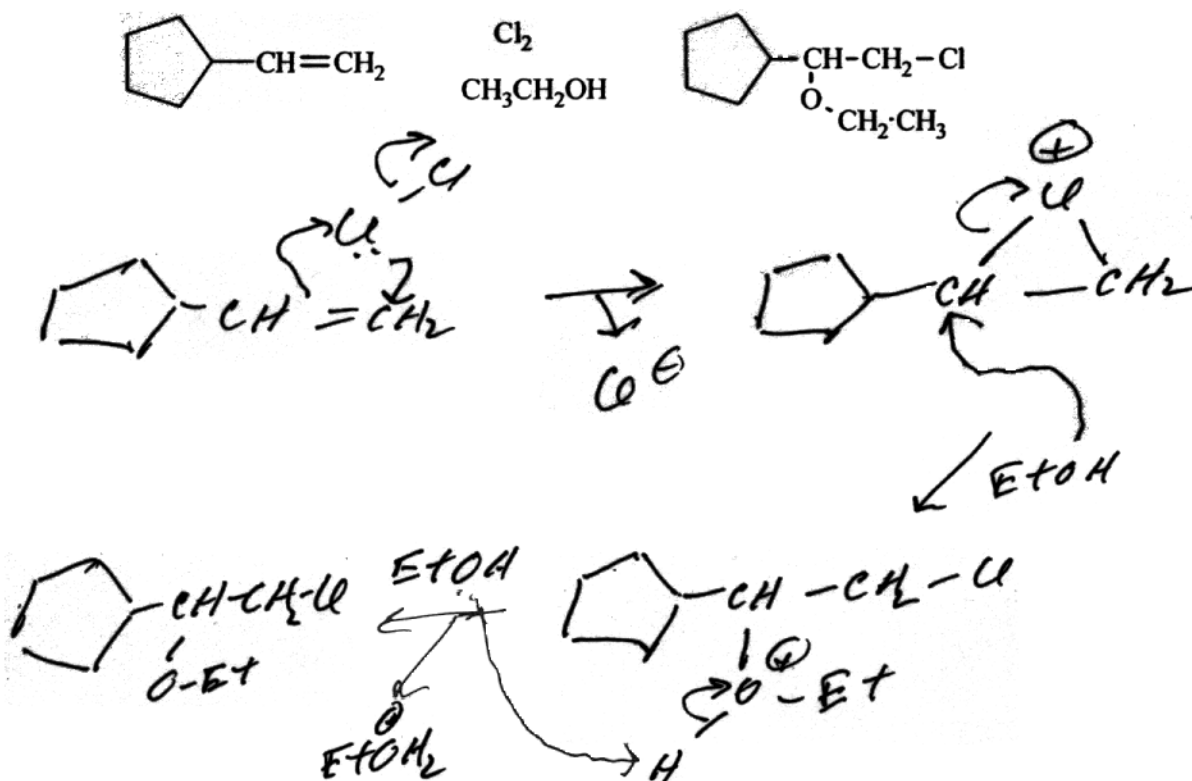
5. (5) The proton NMR spectrum of CH3OH at room temperature consists of two singlets. If the sample is cooled to -70°C , one of the singlets appears as a quartet and the other as a doublet. Account for the appearance of the spectra at these two temperatures.



at -70°C, mutual splitting results in a doublet for CH₃ and a quartet for OH. At r.t., rapid exchange of OH protons averages environments, removes splitting.



9. (10) Write a mechanism for the following reaction. Show all steps clearly, include formal charges where necessary, and use correct electron pushing. (The use of the symbol H^+ is unacceptable.)



1. add Cl_2
2. attack with EtOH
3. deprotonate