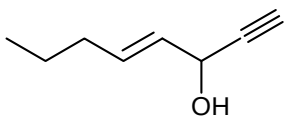
Problem R-04E ($C_8H_{12}O$)

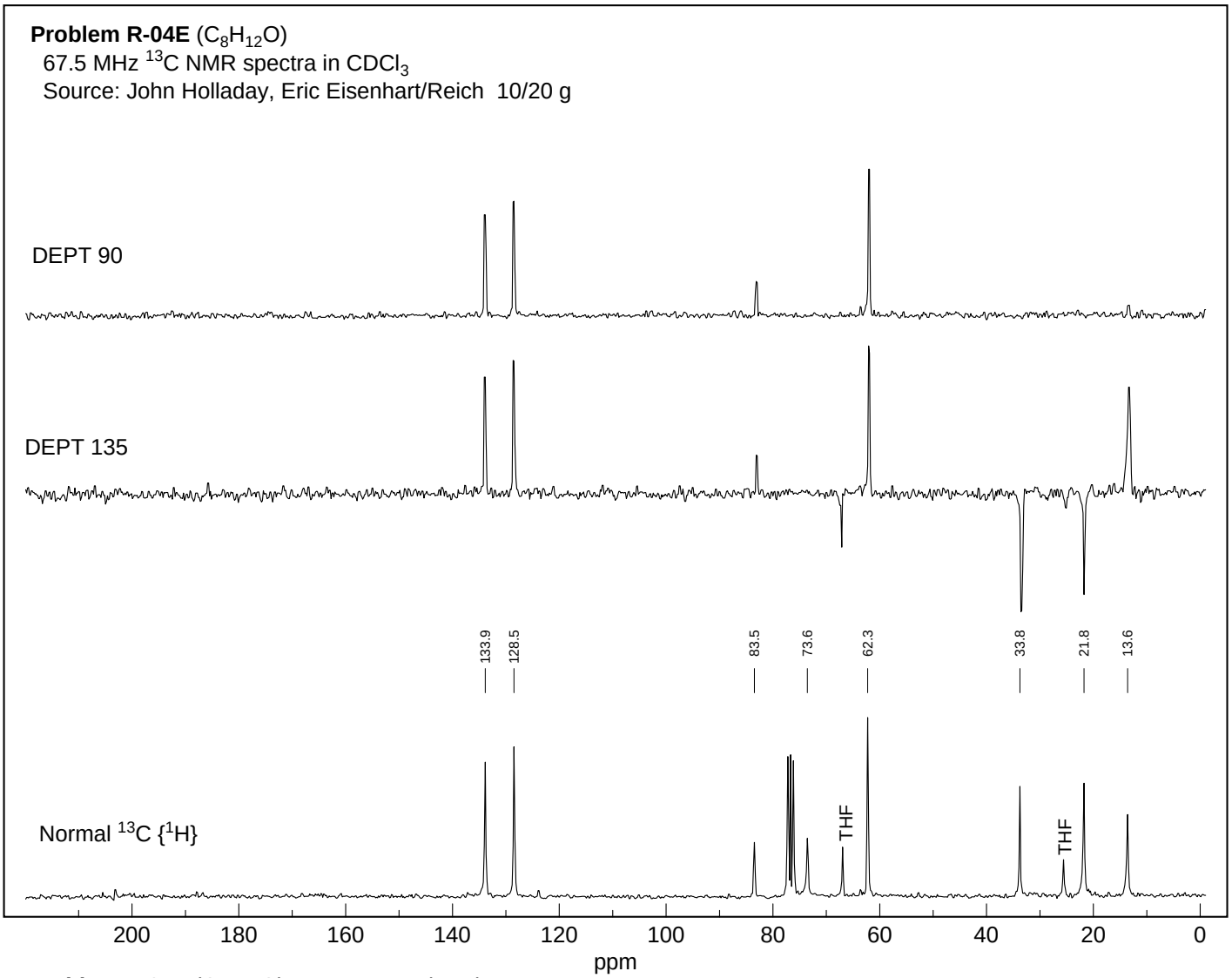
200 MHz ^{1}H NMR spectrum in $CDCl_3$

Source: John Holladay, Eric Eisenhart/Reich 10/20 (digitized hard copy) g



PLT ex-1-2004-05-gq.plt

Problem R-04E ($C_8H_{12}O$)
67.5 MHz ^{13}C NMR spectra in $CDCl_3$
Source: John Holladay, Eric Eisenhart/Reich 10/20 g



Problem R-04E ($C_8H_{12}O$) IR spectrum (neat)
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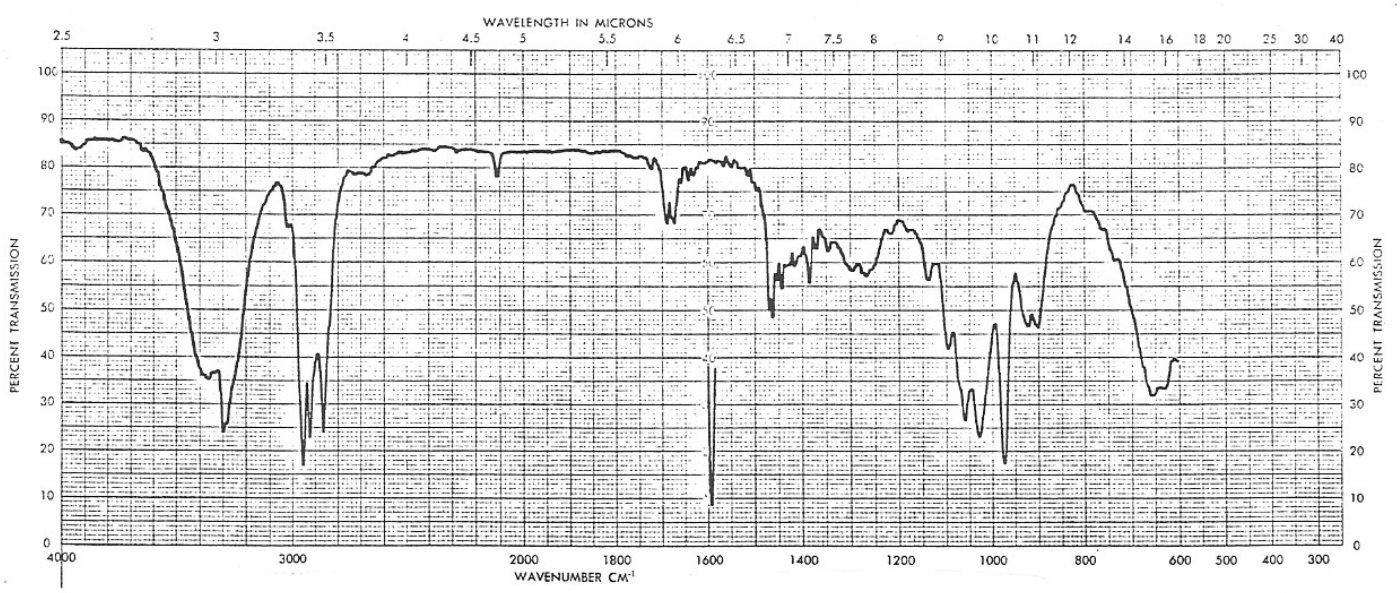

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Problem R-04E ($C_8H_{12}O$). Determine the structure (or part structure) of R-04E from the ^{1}H NMR, ^{13}C NMR and IR spectra provided.

(a) DBE____ (b) What information can you obtain from the IR spectrum (give frequency and interpretation)?

(c) Interpret the ^{13}C NMR spectrum. Identify what kind of carbon each signal corresponds to, and write possible part structures.

No	ppm	Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)	No	ppm	Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)
1	13.6		5	73.6	
2	21.8		6	83.5	
3	33.8		7	128.5	
4	62.3		8	133.9	

(d) Analyze the multiplets between δ 5.5 and δ 6.1 in the ^{1}H NMR spectrum. Report multiplicity, coupling constants and the part structure you could obtain from the signals. Label the part structure with chemical shifts and coupling constants.

(d) Analyze the multiplets between δ 0.8 and δ 2.2 in the ^{1}H NMR spectrum. Report multiplicity, coupling constants and the part structures you could obtain from the signals. Label the part structures with chemical shifts and coupling constants.

(e) Analyze the the signals at δ 2.7 and δ 4.8 in the ^{1}H NMR spectrum. Determine the structure of **R-04E**. If more than one structure is possible, show them, and circle your best choice.

(f) Do a chemical shift calculation for the proton you have assigned to the signal at 4.8. Show your work. What

Problem R-04E ($C_8H_{12}O$). Determine the structure (or part structure) of R-04E from the ^1H NMR, ^{13}C NMR and IR spectra provided.

(a) DBE 3 (b) What information can you obtain from the IR spectrum (give frequency and interpretation)?

4
- nothing strong around 1700 cm^{-1}, so no C=O group
- 2120 cm^{-1} probably a C≡C stretch
- 3300 cm^{-1} - C≡C−H stretch
- 3400 cm^{-1} broad - H-bonded OH
- 1680 cm^{-1} C=C stretch

(c) Interpret the ^{13}C NMR spectrum. Identify what kind of carbon each signal corresponds to, and write possible part structures.

Because of the much larger J_{C-H} alkynyl CH give misleading info in DEPT

No	ppm	Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)	No	ppm	Type of C (e.g. sp^3 CH_2) and/or part structures (e.g. N-CH_2)
1	13.6	C-**C**H_3	5	73.6	C≡**C** (actually C≡**C**-H
2	21.8	C-**C**H_2-C	6	83.5	C≡**C**-H (actually C≡**C**-C)
3	33.8	C-**C**H_2-C	7	128.5	H, H, **C**, sp^2
4	62.3	H, C-**C**-OR	8	133.9	H, **C**, sp^2

5

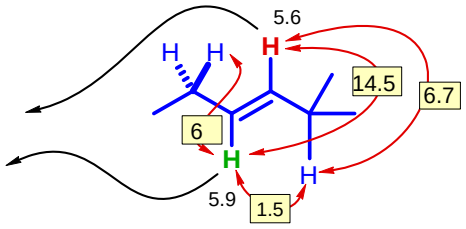
(d) Analyze the multiplets between δ 5.5 and δ 6.1 in the ^1H NMR spectrum. Report multiplicity, coupling constants and the part structure you could obtain from the signals. Label the part structure with chemical shifts and coupling constants.

These are vinyl protons:

δ 5.6 ddt, *J* = 14.5, 6.7, 1.8 Hz

δ 5.6 dtd, *J* = 14.5, 6, 1.5 Hz

5



(d) Analyze the multiplets between δ 0.8 and δ 2.2 in the ^1H NMR spectrum. Report multiplicity, coupling constants and the part structures you could obtain from the signals. Label the part structures with chemical shifts and coupling constants.

$CH_3—CH_2—CH_2—CH$

δ 2.1, apparent q, *J* = 7 (actually a td or dt)

4 δ 1.4, apparent sextet, *J* = 7 Hz (actually tq)

δ 0.9, t, *J* = 7 Hz

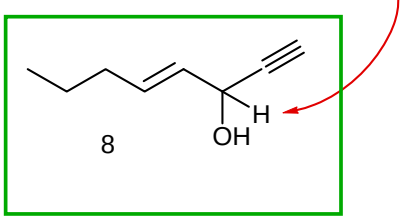
(e) Analyze the the signals at δ 2.7 and δ 4.8 in the ^1H NMR spectrum. Determine the structure of **R-04E**. If more than one structure is possible, show them, and circle your best choice.

2 δ 2.6, d, J=2.5, HC-C≡C-**H**

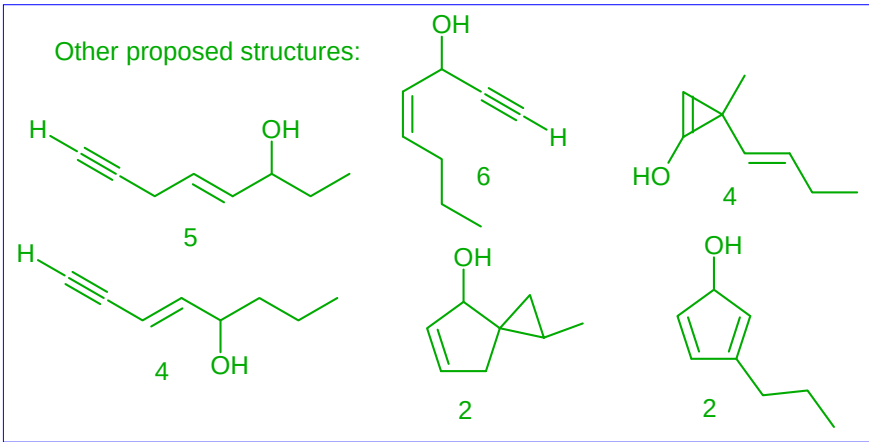
δ 2.8 broad s O-**H**

δ 4.8, ddt, *J* = 6, 1.8. 1.5 Hz

8



Other proposed structures:



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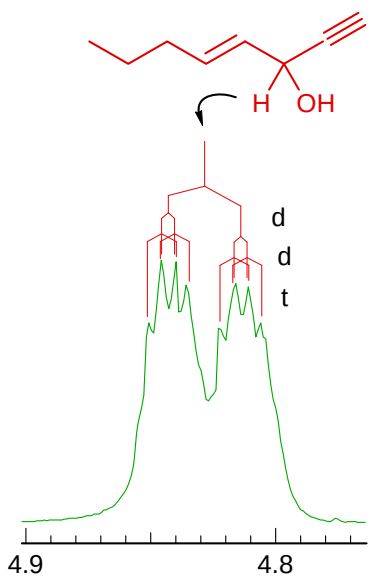

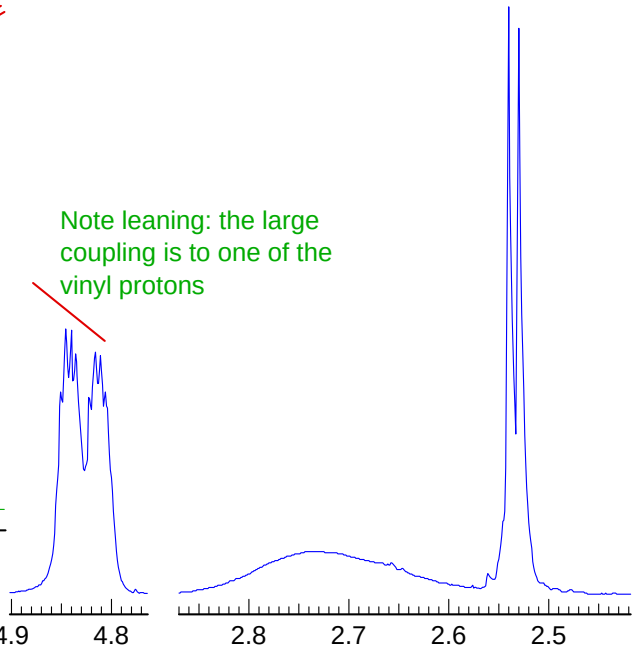

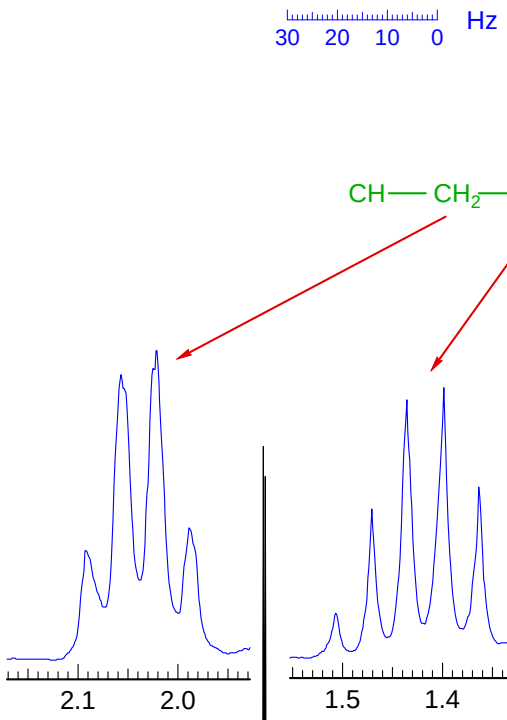

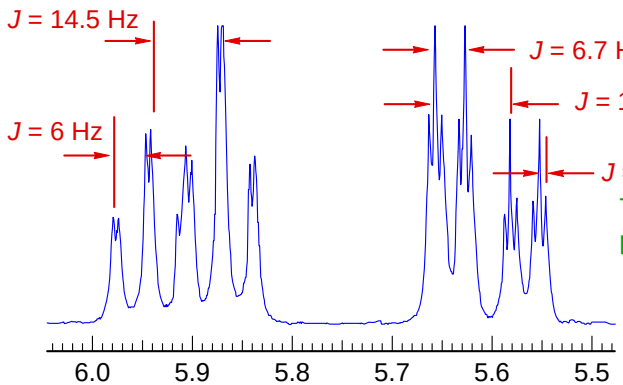

The small coupling of both vinyl protons are ^4J

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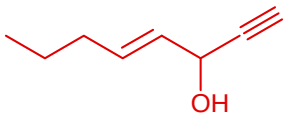
$^2J_{C-H}$ = 50 Hz
-C≡C-H
$^1J_{C-H}$ = 250 Hz

The DEPT experiment is calibrated for J_{C-H} of ca 125 Hz, so the couplings in terminal acetylenes give erroneous results

Actually C≡**C**-H is here
Probably HC=CH
Looks like a C-H, but this is actually C≡**C**-C

DEPT 90
CH CH

DEPT 135
CH CH_3 CH_2 CH_2



133.9 128.5 83.5 73.6 62.3 33.8 21.8 13.6

Normal ^{13}C {^1H}
THF THF

200 180 160 140 120 100 80 60 40 20 0
ppm

Problem R-04E ($C_8H_{12}O$) IR spectrum (neat)
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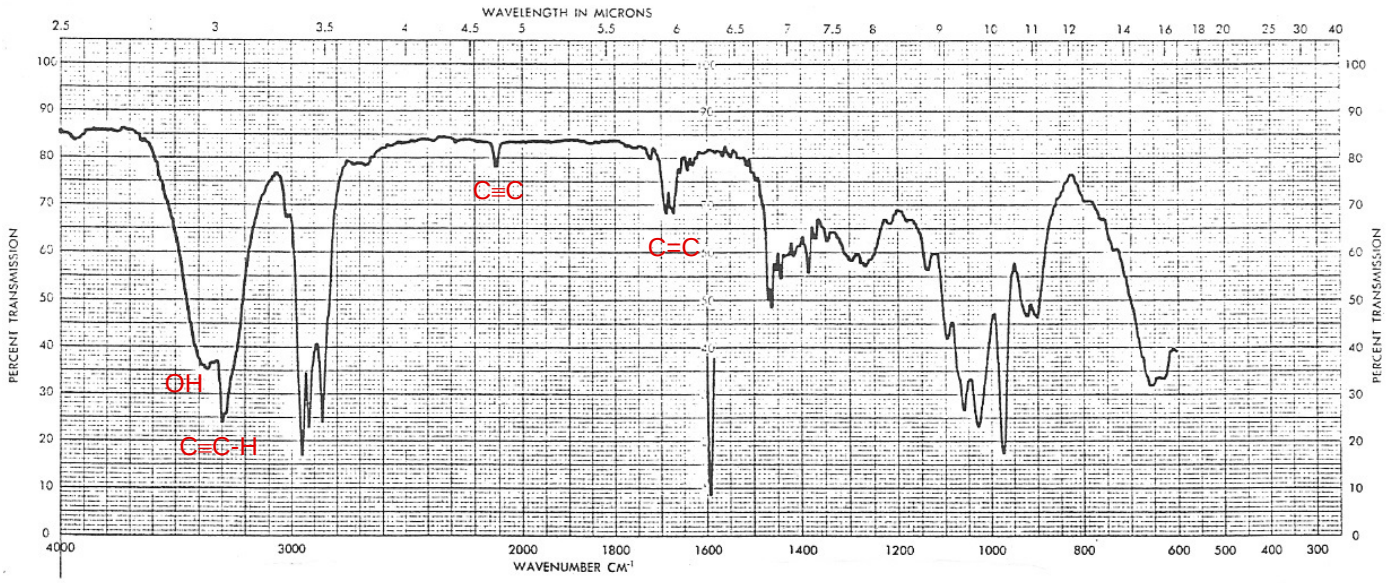
- no C=O



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