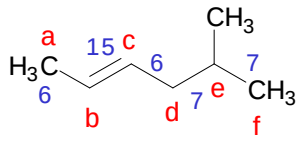
Problem Set 2 Answers

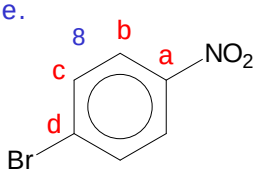
1. Typical ^3J values (in Hz) are given in blue.

(a)



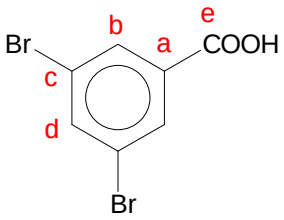
6 ^{13}C & 6 ^{1}H signals
a: d d: dd
b: dq e: t of sextets
c: dt f: d

(b)



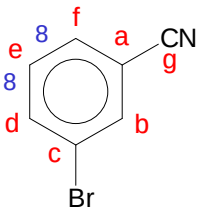
4 ^{13}C & 2 ^{1}H signals
b & c: both d

(c)



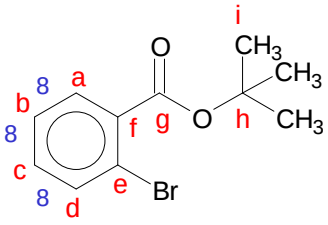
5 ^{13}C & 3 ^{1}H signals
b, d & e: all s

(d)



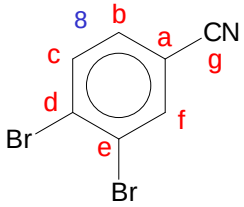
7 ^{13}C & 4 ^{1}H signals
b: s d: d
e: dd (t) f: d

(e)



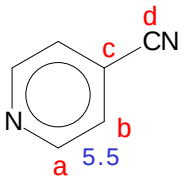
9 ^{13}C & 5 ^{1}H signals
a: d d: d
b: t (dd) i: s
c: t (dd)

(f)



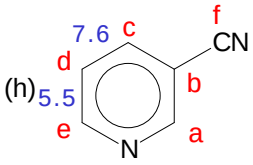
7 ^{13}C & 3 ^{1}H signals
b: d d: d
f: s

(g)



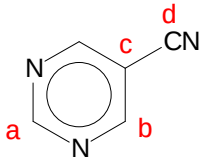
4 ^{13}C & 2 ^{1}H signals
a & b: both d

(h)



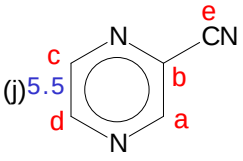
6 ^{13}C & 4 ^{1}H signals
a: s c: d
d: dd (t) e: d

(i)



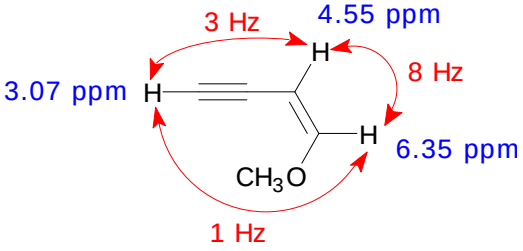
4 ^{13}C & 2 ^{1}H signals
a & b: both s

(j)

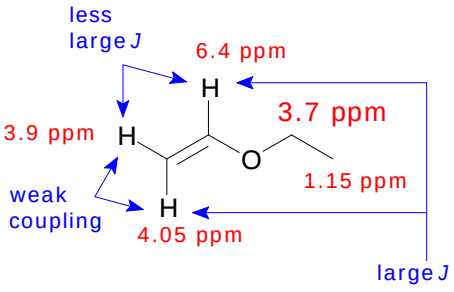


5 ^{13}C & 3 ^{1}H signals
a: s c: d
d: d

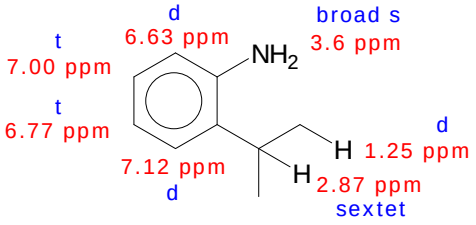
2.



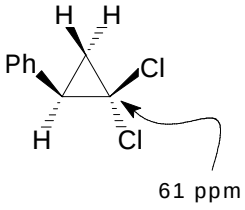
3. (a)



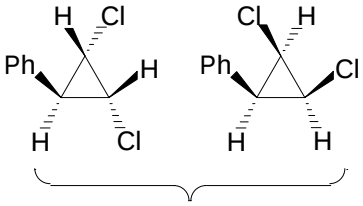
(b)



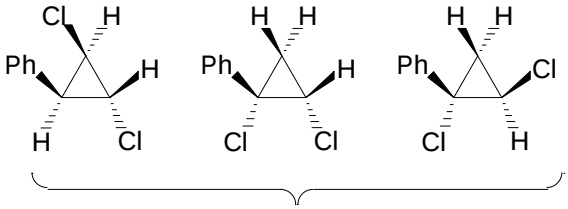
3. (c) The formula $C_9H_8Cl_2$ suggests 5 elements of unsaturation and the multiplet worth 5H in the aromatic region argues for a phenyl group, which accounts for 4 elements of unsaturation. The remaining element of unsaturation can be due to a double bond or a ring, but there is no CH_3 group (required of a -CCl=CCl-CH_3 moiety) and no sign of alkenyl H (required of any other alkenyl moiety), which leaves a ring as the likely source. With only three carbons unaccounted for, this means a cyclopropane. There are 6 isomers (+ enantiomers thereof).



this fits

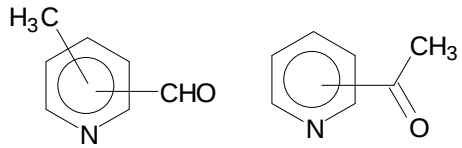


only 2 aliphatic ^1H signals expected in these cases

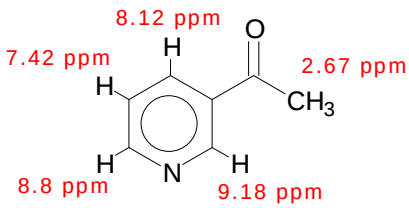


^1H & ^{13}C chemical shifts are not consistent with these structures, especially of CH next to Cl (expected at lower fields in both ^1H & ^{13}C spectra)

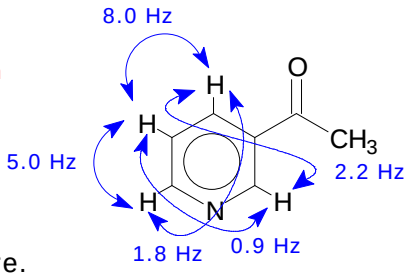
(d) The formula C_7H_7NO suggests 5 elements of unsaturation and the multiplet worth 3H in the aliphatic region argues for a CH_3 group. The weak ^{13}C peak at 192 ppm is consistent with a C=O group, which accounts for 1 element of unsaturation and leaves a C_5H_4N fragment to account for 4 elements of unsaturation. The remaining ^1H signals are all in the aromatic region (one might be aldehydic), so we can postulate an aromatic moiety to account for the remaining 4 elements of unsaturation. With a C_5H_4N fragment, this means a pyridine, either singly substituted with an acetyl group or doubly substituted with a CH_3 and a formyl.



The ^{13}C spectrum suggests 4 H-bearing aromatic carbons and this fits an acetylpyridine.

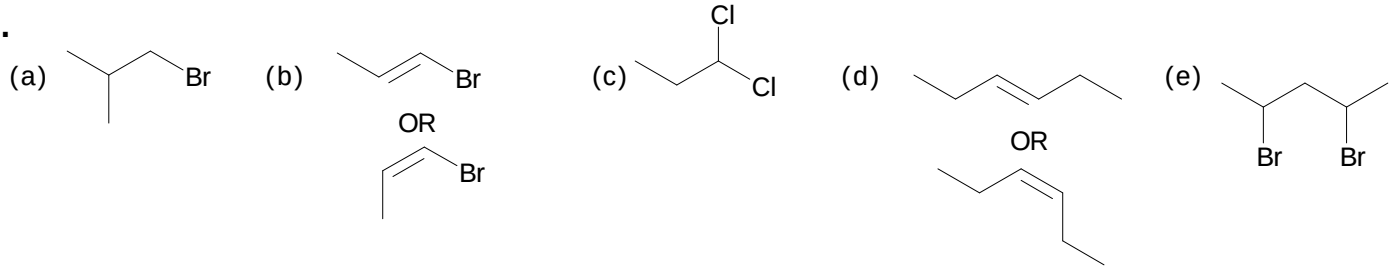


The chemical shifts are also consistent with this structure.

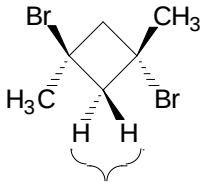


The number of signals and the coupling constants are consistent with 3-acetylpyridine. An additional strong coupling would have been expected of 2-acetylpyridine, and 4-acetylpyridine would show only 2 aromatic signals.

4.

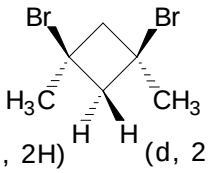


5.



(s, 4H)
homotopic

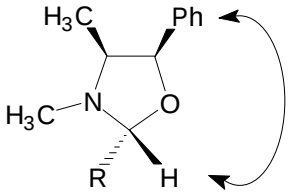
isomer A



(d, 2H) (d, 2H)
diastereotopic

isomer B

6.



deshielding

Because the Ph is end-on, it is expected to deshield the H when it is on the same face of the oxazolidine ring, the minor isomer giving the downfield signal (6.2 ppm) has the CH_3 group *trans* to Ph while the major isomer giving the upfield signal (5.5 ppm) has CH_3 group *cis* to Ph.