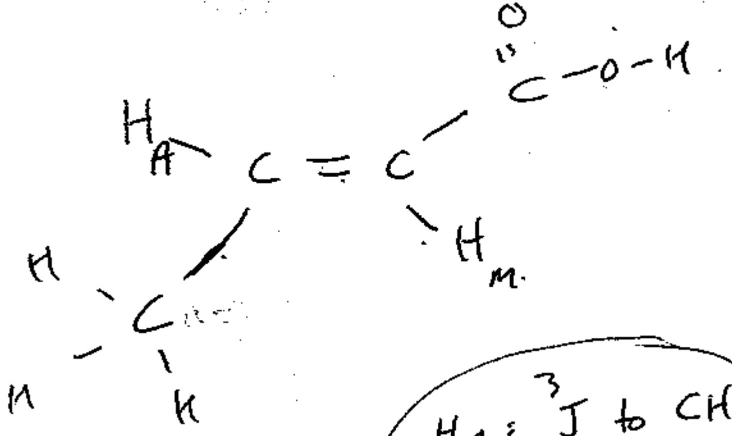
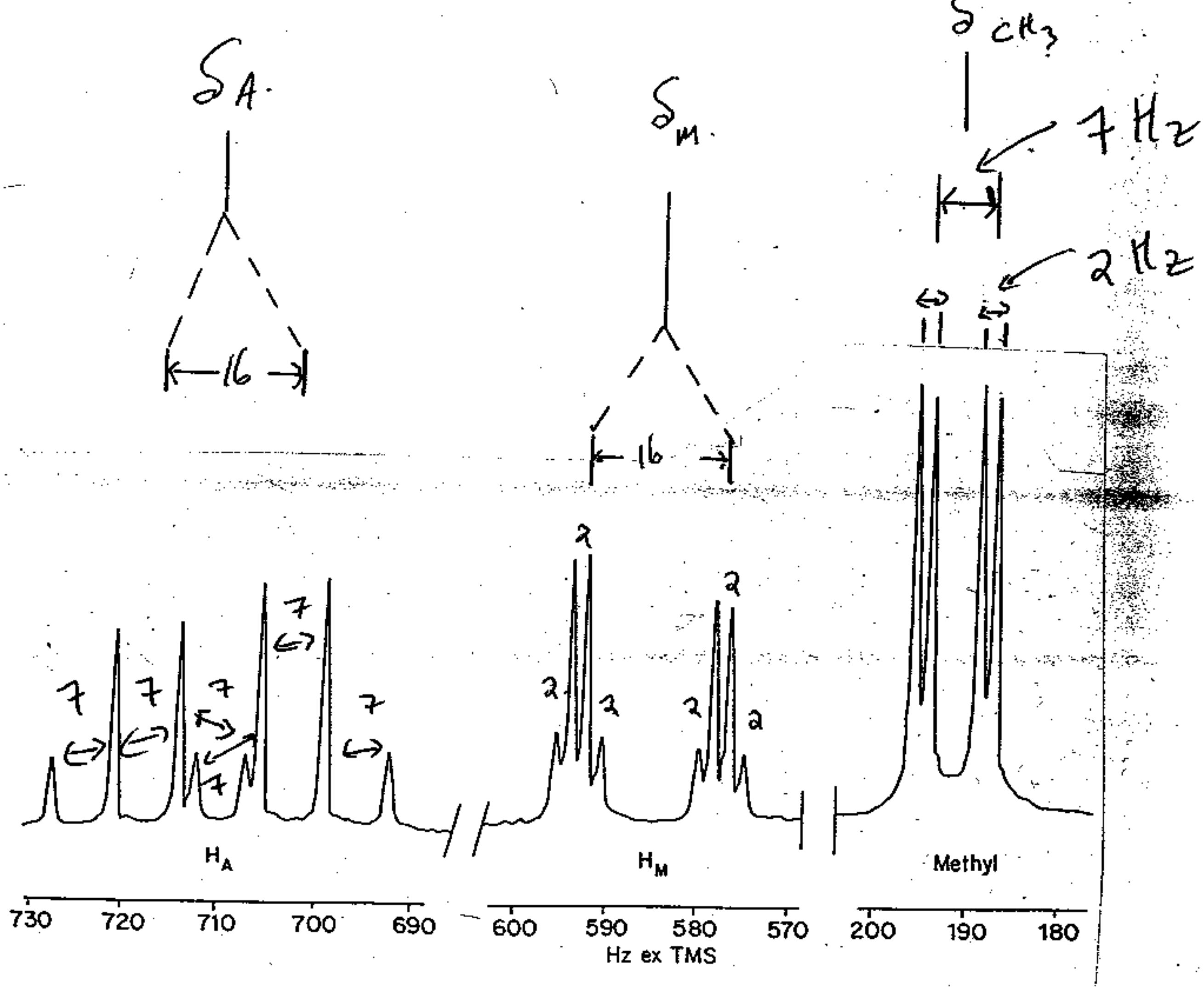
1



CH_3: ^4J to H_M
^3J to H_A

H_A: ^3J to CH_3
^3J to H_M

H_M: ^4J to CH_3
^3J to H_A



1.

(i) Scale 10 Hz ≙ 13 mm

∴ 1 mm = 0.77 Hz ②

CH_3 region; smaller J = 2mm (occurs twice)

∴ J = 1.54 Hz ②

large splitting: ~ 9 mm

∴ J = 9 × .77 = 6.9 Hz ②

Hm region: smaller J (occurs 6 times)

~ 2 mm ∴ J = 1.54

large J (occurs 4 times) = 20 mm

∴ J = 15.4 Hz ②

HA region smaller J (occurs 6 times)

= 9 mm ∴ J = 6 9

& large J (occurs 4 times) = 20mm or 15.4 Hz

Thus, since ^4J is the smallest,

coupling from H_M to the CH_3 is ① <u>1.54 Hz</u>

And CH_3 also couples via ^3J to H_A ①

this must be 6.9 Hz.

Finally, H_A + H_M (trans H's on C=C)

couple via ^3J of ≈ 15.4 Hz ①.

(ii) Since spectrum is 1st order, can just use the centre of each multiplet to get chemical shift. ①

∴ for CH_3, centre is ≈ 190 Hz or 1.9 ppm.

for H_M, centre is ≈ 585 Hz or 5.85 ppm ①

for H_A centre is ≈ 710 Hz or 7.10 ① ppm

(iii) OH will be around 12 ppm. ①

Total = <u>15</u> marks.

2. C_8H_7OCl

sites of unsat'n $= 9 - \frac{7H}{2} = 5$ ①

^{13}C Shows only 6 C's ∴ Some Symmetry ①

^{13}C-DEPT 90, CH, CH, CH_3 ①

So 3 quaternary (non protonated c's)
peak at 197 (Ketone) ②

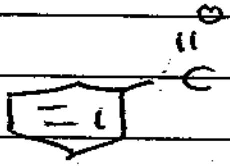
^1H NmR: 3H singlet (CH_3) not coupled. ①

4 H's (2 pairs) at ~ 7.5 ppm

∴ 4 aromatic H's

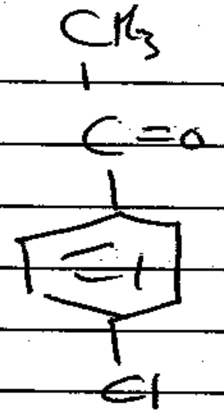
①

∴ must have a  ring

IR 1690 - looks like  ②

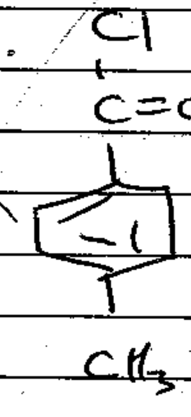
also CH_3, So all C's accounted for

So, best structure is



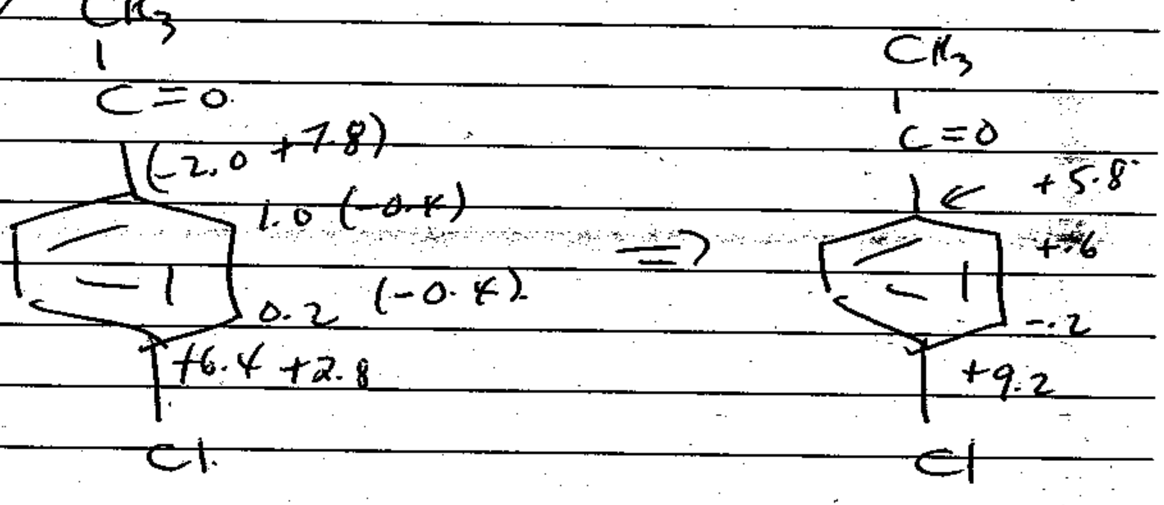
⑥

⑨ for [illegible]:



IR for acid halide is ~ 1770 cm⁻¹

Also: try to use ¹³C subs effects (Table A8-7)



Verifies

∴ Predicted shifts

128.5 + 5.8 = 134.3

128.5 + .6 = 129.1

128.5 - .2 = 128.3

128.5 + 9.2 = 137.7

VERY CLOSE TO OBS'D!!

3. COSY

(i) Starting point: doublet @ ~ 6.0, should be H-2 ②

(ii) Correlates to H-3 @ 6.8 ①

(iii) 6.8 correlates to peak @ 2.4 ∴ H-4 (complex) ①

(iv) 2.4 correlates to 5.2 ∴ H-5 is at 5.2 ①

(v) 5.2 correlates to 5.5 ∴ H-6 at 5.5 ①

(vi) 5.5 couples to 5.6 ∴ H 7 at 5.6 ①

(vii) 5.6 couples to 2.0 ∴ H. 8 at 2.0 ①

(viii) 2.0 correlates to 1.4 ∴ H-9 at 1.4 ①

(ix) mess at 1.3 – must be H10 + 11 – correlates to C12 at 1.0 ①

⑳ ⑩

^{13}C: order ⟶

3, 7, 6, 2   5, 8, 4   (9, 10, 11)   12

⑧ | | | | | | | (indist) |

②   ⑧

(2 3.5) – Diastereotopic H's on C-4.

Solut Cop.

#3

Quiz #2

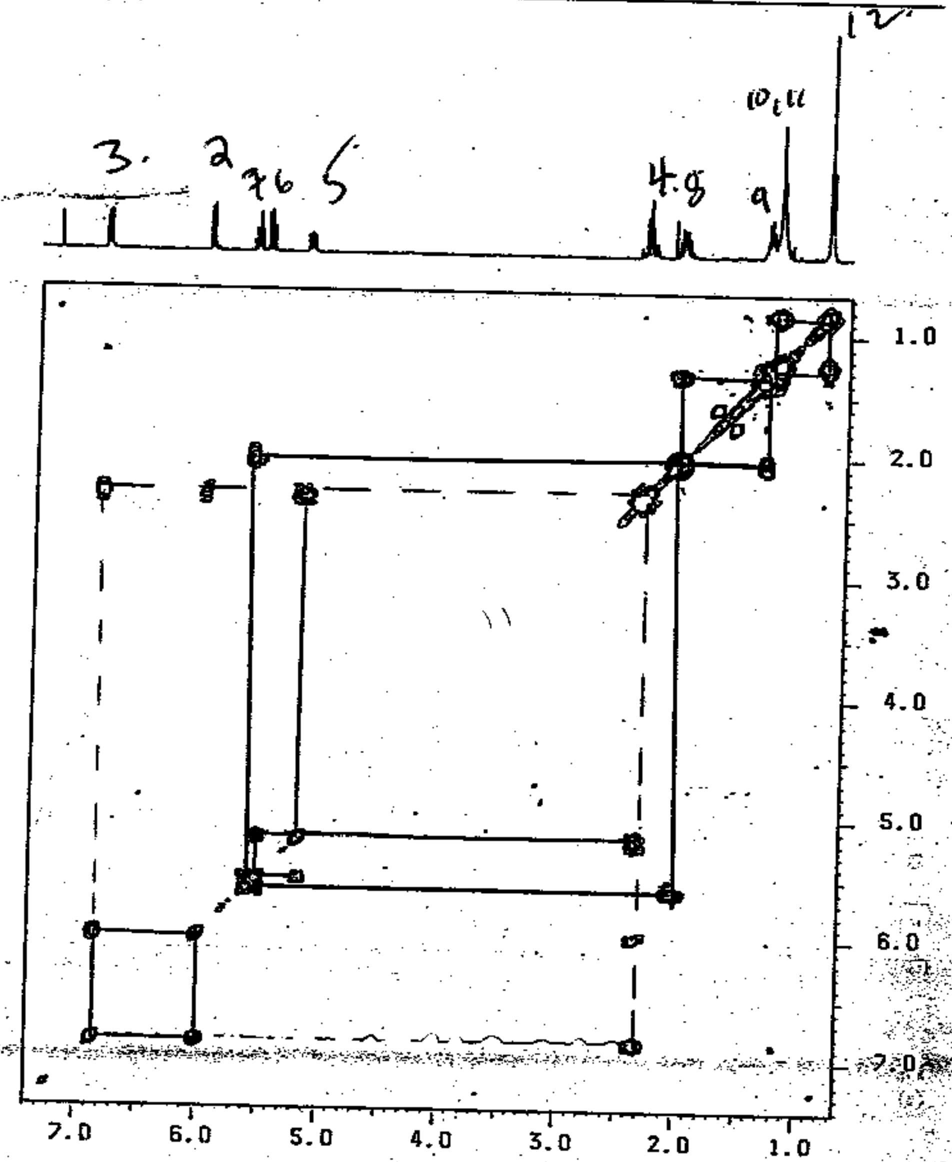


Fig. 3.2.3. H,H COSY spectrum of 2.

Fig. 3.2.4. H,C COSY and DEPT spectra of 2; the ^{13}C NMR spectrum contains an additional signal at $\delta = 164.5$ (C).