

Chemistry 225

**Final Examination**

Time: 2.5 hr.

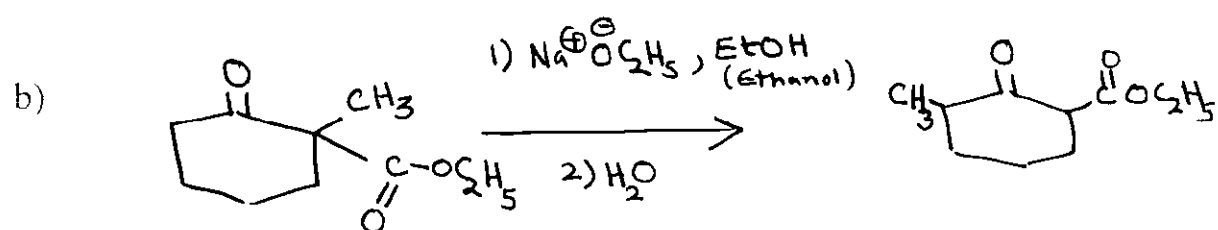
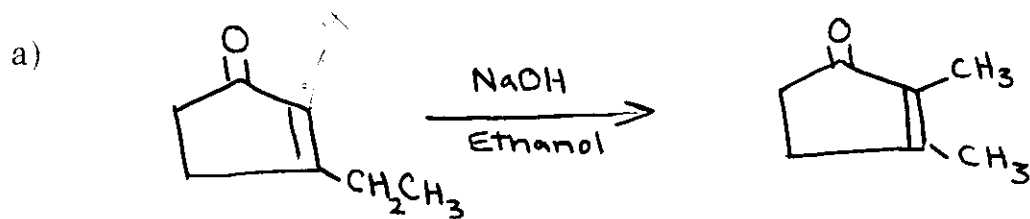
February 8, 1996  
M.J.Haddadin

- 15 -1.
- 15 -2.
- 20 -3.
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150 pt.

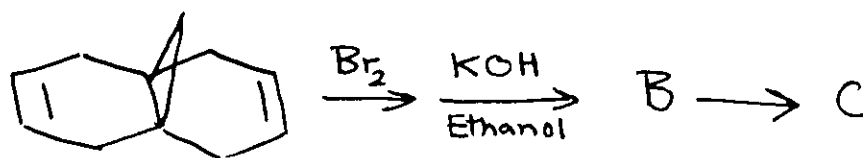


1. Give a reasonable mechanism to explain the following transformation:



2) The infrared spectrum of compound A gives a carbonyl band at  $1830\text{ cm}^{-1}$ . The proton NMR spectrum consists of a broad singlet at  $\delta$  7.34. The  $\text{C}^{13}$  NMR consists of four lines all in the  $\delta$  100-200 region. The important ions in the mass spectrum are  $m = 63$  (48%),  $64$  (100%),  $92$  (56.2%),  $136$  (75.5%),  $137$  (6.1%). Give the structure of compound A.

3. A Chemistry 225 student believed that one of his/her unknowns is compound A which reacted readily with Br<sub>2</sub>. further heating of the bromide product with hot KOH/ethanol yielded compound B which spontaneously converted to C.

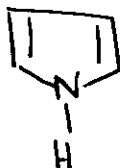


a) Give the structures of B and C which contain no Br.

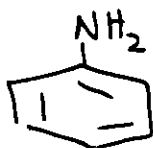
b) Why do the two protons of the bridged methylene show at  $\delta(-0.5)$  in NMR spectrum of C? Be brief.

c) Where do you expect the rest of the protons of C to appear in the NMR spectrum? Give an estimated chemical shift.

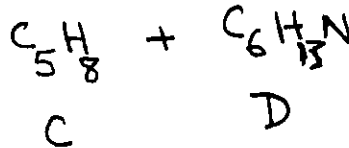
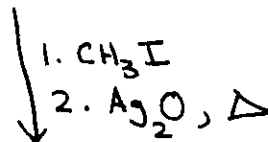
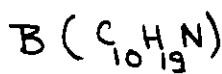
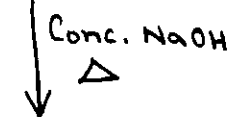
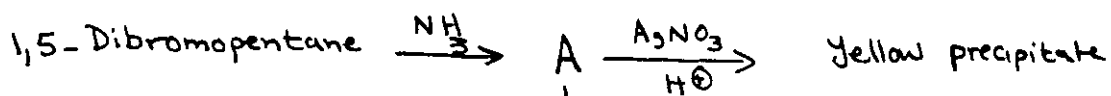
4. a) Which of the following compounds is water soluble and which is (are) not?



b) Which, if any, of the following compound's U.V. spectrum will be dramatically effected by protonation and why? Be brief.

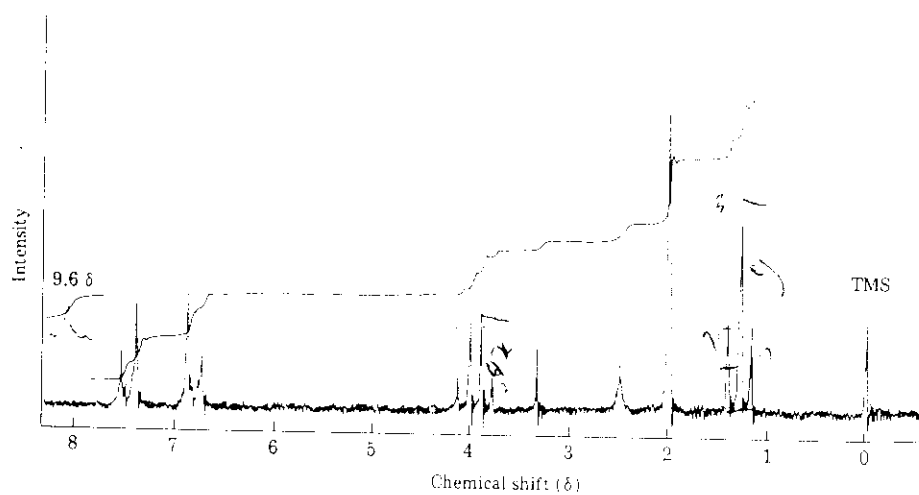
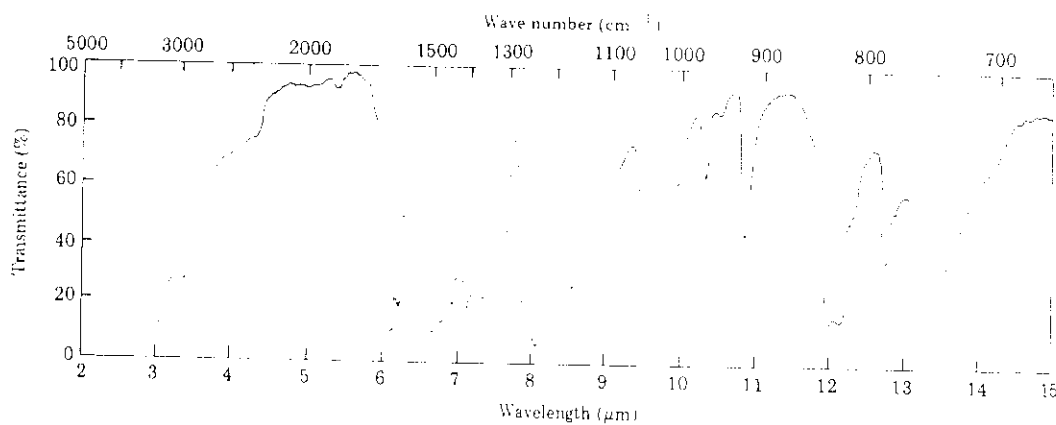


c) Consider the following reactions and give the structures of **A-D**.



- B: Decolorizes Br<sub>2</sub>/CCl<sub>4</sub>,  
Dissolves in 5% HCl
- C: Decolorizes Br<sub>2</sub>/CCl<sub>4</sub>
- D: Dissolves in 5% HCl  
Does not react with HNO<sub>2</sub>

5. A neutral compound ( $C_{10}H_{13}NO_2$ ) yields  $C_8H_{11}NO$  upon warming with aqueous hydroxide. Heating  $C_8H_{11}NO$  with HI gives  $C_6H_7NO$  which upon oxidation yields p-benzoquinone. The NMR and IR of  $C_{10}H_{13}NO_2$  are shown below. Give the structures of  $C_{10}H_{13}NO_2$ ,  $C_8H_{11}NO$  and  $C_6H_7NO$ .



6. Compound A ( $C_{10}H_{12}O$ ) which, among other peaks in its proton NMR spectrum, has a singlet at  $\delta 2.2$  (3H). Upon heating at  $200^\circ C$  it was converted to a base soluble B ( $C_{10}H_{12}O$ ). Heating of B with NaOH followed by acidification gave C ( $C_{10}H_{12}O$ ). Treatment of B with a solution of aniline, sodium nitrite and HCl at  $5^\circ C$  and adjustment of the pH of the solution to 9, followed by acidification gave a bright yellow product which upon reduction with Sn, HCl yielded D ( $C_{16}H_{18}ON_2$ ). Ozonolysis of B followed by reduction of the ozonide gave E ( $C_9H_{10}O_2$ ). E reacted with ammoniacal silver nitrate to give, after acidification, F which upon heating with HCl yielded G ( $C_9H_8O_2$ ). F showed the same singlet (3H) of A and dissolved in hot 5% NaOH.

Give the structures of A-G.

7. A compound (A), containing only carbon, hydrogen, and oxygen, was found to react with acetyl chloride but not with phenylhydrazine. Oxidation with periodic acid converted it to a new compound (B), which reduced Tollens but not Fehling's reagent. Treatment of B with potassium cyanide in aqueous ethanol converted it to a new compound (C), which gave positive tests with acetyl chloride and phenylhydrazine. Oxidation of C with Fehling's solution or nitric acid converted it to a yellow compound (D) that yielded a derivative with o-phenylenediamine. When D was treated with hydrogen peroxide it yielded an acid (E) having a neutralization equivalent of  $151 \pm 1$ . Catalytic hydrogenation of C or D produced the original compound (A). The nmr spectrum of compound B (in  $\text{CDCl}_3$ ) showed  $\delta$  3.42, 3H, s; 6.9, 2H, d ( $J = 10$  Hz); 7.56, 2H, d ( $J = 10$  Hz); 9.81, 1H, s.

Give the structures of A-E





8. A compound (I), giving positive tests for nitrogen and chlorine, was insoluble in water and hydrochloric acid but soluble in sodium bicarbonate solution. A neutralization equivalent of  $210 \pm 2$  was obtained. Compound I reacted with acetyl chloride but not with hot alcoholic silver nitrate. The acetyl derivative (II) had a neutralization equivalent of  $253 \pm 2$ . Boiling alkali liberated ammonia from I, and acidification of the resulting solution precipitated a new acid (III), which had a neutralization equivalent of  $115 \pm 1$ . Compound III contained chlorine but no nitrogen. When compound III was boiled with potassium permanganate solution, a new compound having the same solubility characteristics as I was produced that still contained chlorine and gave a neutralization equivalent of  $81 \pm 1$ .

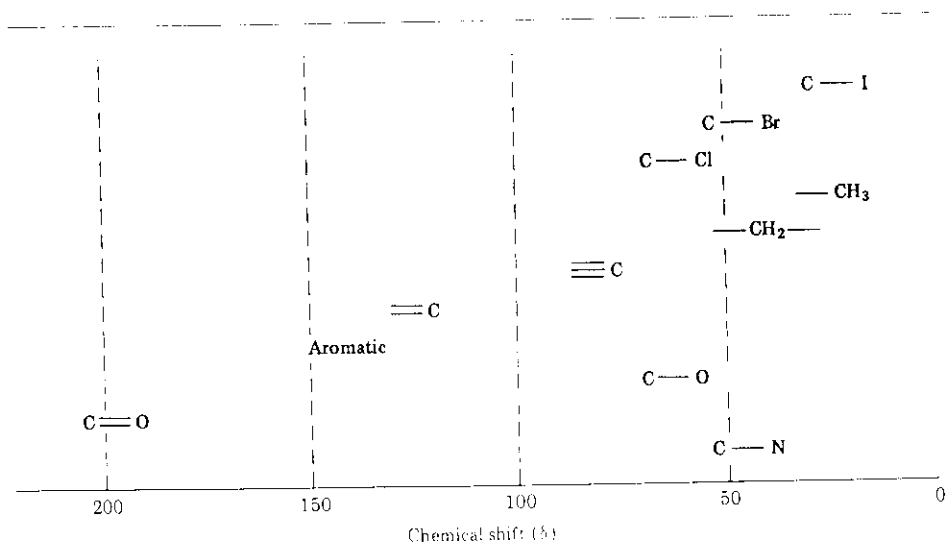
Compound IV (neutralization equivalent 71) could be chlorinated to give the compound of neutralization equivalent 81; compound IV yielded an nmr spectrum ( $\text{CDCl}_3$ , DMSO- $d_6$  solvent) displaying  $\delta$  7.57, 1 H, t ( $J = 7$  Hz); 8.18, 2 H, d ( $J = 7$  Hz); 11.2, 3 H, bs.

The ir spectrum of I (in Nujol) showed, among other bands, strong absorptions at  $1779 \text{ cm}^{-1}$  (5.62  $\mu$ ) and  $1712 \text{ cm}^{-1}$  (5.84  $\mu$ ).

Give the structures of I - IV.

TABLE 12.2 Carbon-13 NMR chemical shift correlations

Type of carbon	Chemical shift ( $\delta$ )	Type of carbon	Chemical shift ( $\delta$ )
C—I	0–40	=C	100–150
C—Br	25–65	C—O	40–80
C—Cl	35–80	C=O	170–210
—CH <sub>3</sub>	8–30		110–160
—CH <sub>2</sub> —	15–55	C—N	30–65
 CH	20–60		
$\equiv$ C	65–85		

Figure 12.6. Chemical shift correlations for <sup>13</sup>C NMR.