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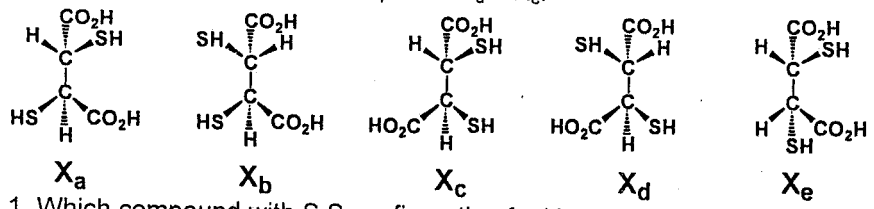
(一) (6 pts, 2 pts each) For compound X_a – X_e:



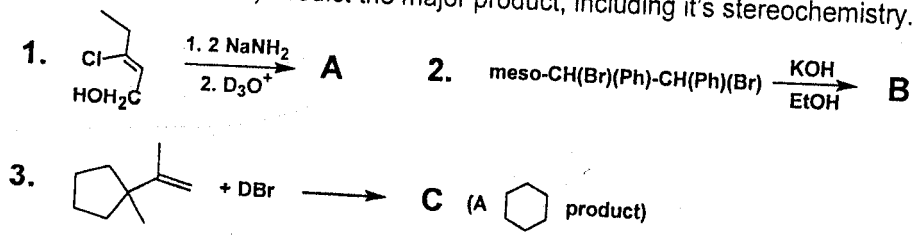
X_a　X_b　X_c　X_d　X_e

1. Which compound with S,S configuration for it's charility centers?　A.X_a B.X_b C.X_c D.X_d E. X_e
2. Which compound is a meso compound (Probably more than one)?　A.X_a B.X_b C.X_c D.X_d E. X_e
3. If X_c with $[\alpha]_D$= -20°, what's the specific rotation of X_a?　A.-20 B.+20 C.-10 D.+10 E.0

(二) (12 pts, 2 pts each)

1. Which reactants with highest reaction rate with Base?
   A. $PhCH_2CH_2Br$ B. $PhCH_2CD_2Br$ C. $PhCD_2CH_2Br$ D. all the same
2. Which nucleophiles with the highest reactivity order in the S_N1 reaction.
   A. HF B. HCl C. HBr D. HI E. all the same
3. Which solvent with the highest reaction rate in the S_N1 reaction.
   A. Ethanol B. methanol C. CH_3CN D. H_2O E. all the same
4. Using a 200 MHz ^1H NMR instrument, if a H show a triplet at δ 1.10 and 1.08 and 1.06 ppm. Calculate it's coupling constant.　A. 2 Hz B. 4 Hz. C. 6 Hz D. 8 Hz E. 10 Hz
5. (Continue from 4) Where will this triplet peak show up (δ:ppm) at a 400HMz ^1H NMR instrument?
   A.1.10,1.09,1.08 B.1.09,1.08,1.07 C.1.08,1.07,1.06 D.1.07,1.06,1.05
   E.1.10,1.08,1.06 F.1.09,1.07,1.05 G.1.08,1.06,1.04 H.1.07,1.05,1.03
6. How many total of peaks (if only the J^1 splitting observed) will show up for $CH_3CH_2CO_2CH_2NH_2$ in a ^{13}C-^1H coupling of ^{13}C NMR.　A.4 B.6 C.8 D.9 E.10 F.11 G.12 H.13

(三) (6 pts, 2 pts each) Predict the major product, including it's stereochemistry.



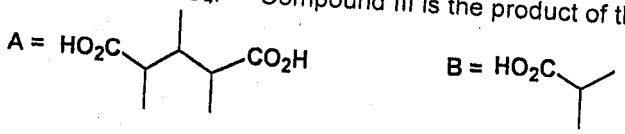
參考用

(四) (6 pts, 3 pts each) s=singlet, d=doublet, t=triplet, q=quartet, m(7)=7 splitting.

1. Propose a structure for **$C_8H_{19}N$** that fits the following ^1H NMR data:
   δ 3.5(2H,q,*J*=7Hz), 3.4(2H,m(7),*J*=6Hz),1.5(6H,d,*J*=6Hz), 1.4(3H,t,*J*=7Hz)
2. Propose a structure for **C_5H_8O** that fits the following ^1H NMR data:
   δ 6.4(1H,*dq*,*J*=14&1.2Hz), 5.0(1H,*dq*,*J*=14&1.5Hz), 2.25(3H, multiplet,*J*=1.2~1.5Hz), 2.15(3H,s)

(五) (6 pts) Suggest structures for compounds I - III. (2 pts each)

Compound I: **C_8H_{14}** only reacts with 1 mol equiv of H_2 and after treatment with acidic $KMnO_4$ gives the dicarboxylic acid A (see below). Compound II (**isomer of I**) reacts with 2 mol equiv of H_2, but yields only B after treatment with acidic $KMnO_4$. Compound III is the product of the *hydroboration* of II



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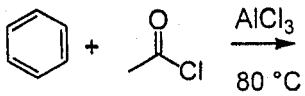
(六) (8 pts, 4 pts each) 1. Organic Syntheses; more than one step is required.
Transformation of **C_6H_5-CH=CH_2 into *cis* C_6H_5-CD=CD-CD_3.**

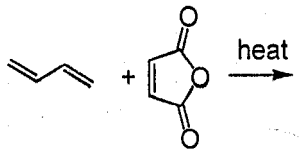
2. Show the details of the reaction mechanism (using arrow or half arrow for the electron flow) for the butyl branch formation during the radical polymerization of ethylene.

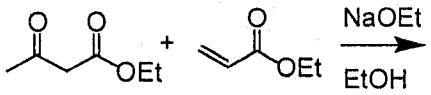
(七) (6 pts) 1. (2 pts) Calcaulate the ring strain (kJ/mol) in cyclobutane.
The heat of combustion (kJ/mol) for Cyclobutane: 2741　Butane: 2875　Pentane: 3535

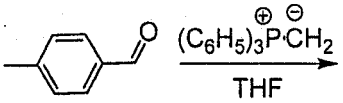
2. (4 pts) Draw the two conformers of *cis-1-tert-butyl-4-isopropylcyclohexane. CIRCLE* the more stable one (2 pts) and calculate by how much kJ/mol that it is favored than the other? (2 pts)
Using the following data (kJ/mol): H–C-C–H eclipsed interaction: 4 ; CH_3–C-C–H eclipsed interaction: 6 CH_3–C-C–CH_3 gauche interaction: 3.8 ; One strain of 1, 3-R-H diaxial interaction in monosubstituted cyclohexane: CH_3=3.8; CH_2CH_3 = 4.0; $CH(CH_3)_2$ = 4.6; $C(CH_3)_3$ = 11.4

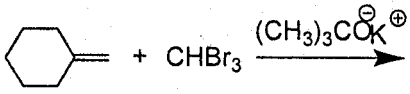
(八) (18 pts) Give the major product, with appropriate stereochemistry, for each of the following transformations:

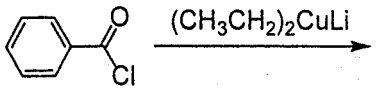
(1). 

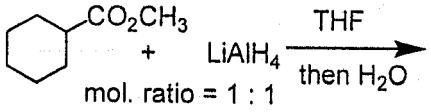
(2). 

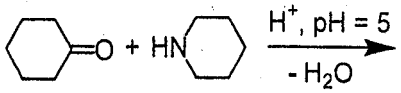
(3). 

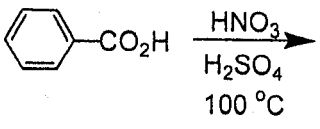
(4). 

(5). 

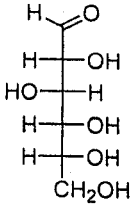
(6). 

(7). 

(8). 

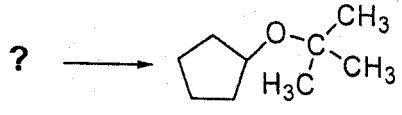
(9). 

(九) (3 pts) The Fischer projection of D-Glucose is shown below:



D-Glucose (a) Draw its chair form of α-D-Glucopyranose.

(十) (3 pts) How would you prepare the following ethers from alcohols?



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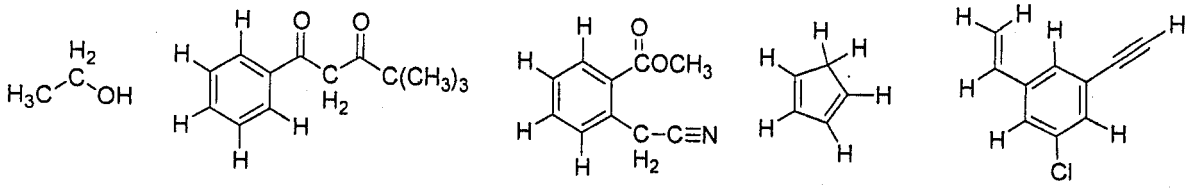
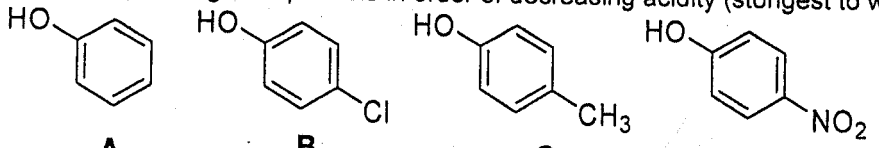
(十一) (10 pts) Identify (circle) all the acidic hydrogens (pKa ≤25) in the following molecules.

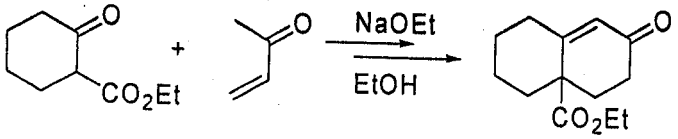


(十二) (2 pts) Arrange the phenols in order of decreasing acidity (stongest to weakest).

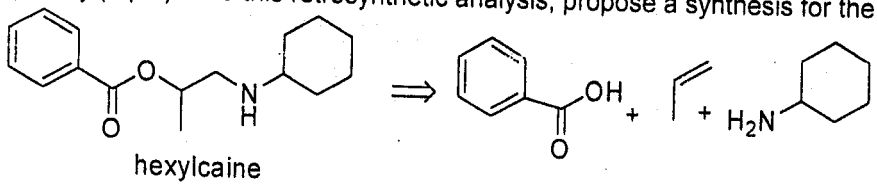


A　　B　　C　　D

(十三) (4 pts) Propose a mechanism for this transformation. Please draw the intermediates and arrows of electron flows. (4 pt)

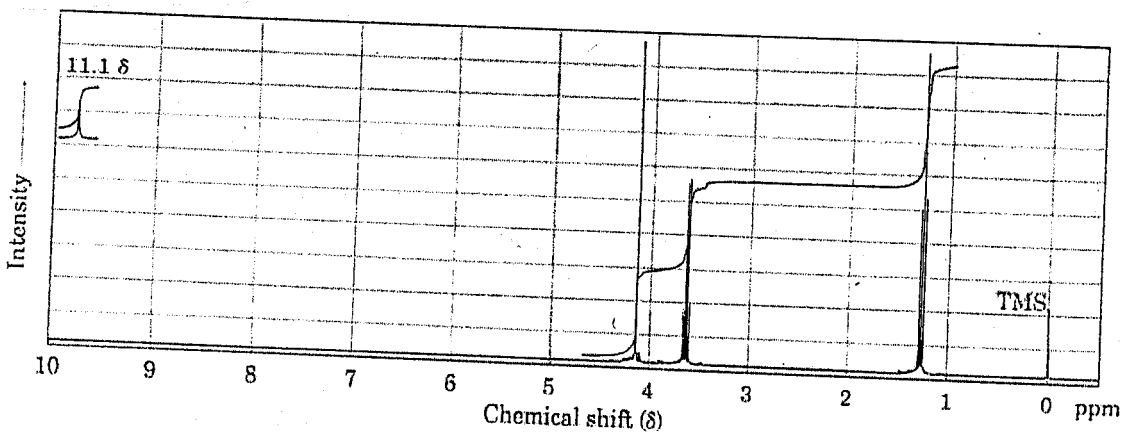


(十四) (5 pts) Give this retrosynthetic analysis, propose a synthesis for the hexylcaine.



hexylcaine

(十五) (5 pts) Compound A, $C_4H_8O_3$, has infrared absorptions at 1710 and 2500 to 3100 cm^{-1} and has the ^1H NMR spectrum ahown. Propose a structure for A.



參考用