

## M.Sc. (Chemistry) Sem-II

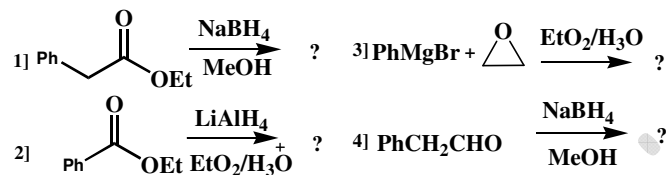
### Question Bank

#### CHO- 4203 (Synthetic organic chemistry and Spectroscopy)

#### Section I

##### A. Objective questions

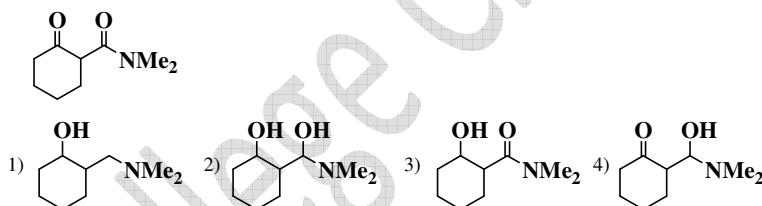
1) Which of the following reaction does NOT give a primary alcohol?



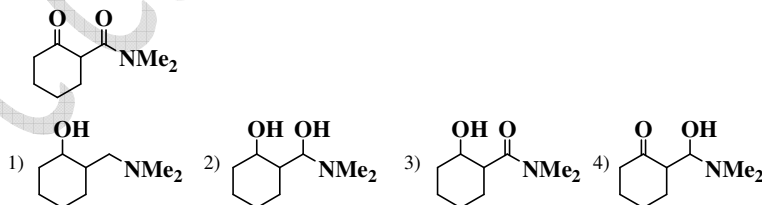
2) Which is unreactive in hydride reduction with  $\text{NaBH}_4$ ?

- 1)  $\text{CH}_3\text{CHO}$  2)  $\text{H}_3\text{COCH}_3$  3)  $\text{H}_3\text{CCOOCH}_3$  4)  $\text{PhCHO}$

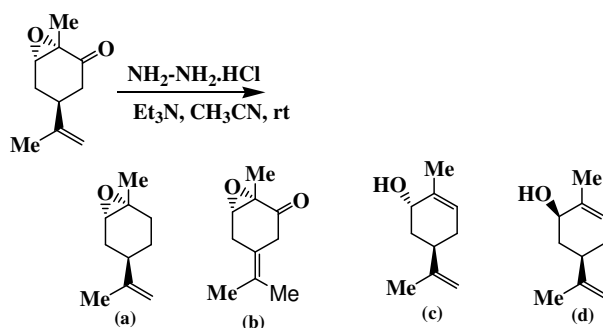
3) Which is the main reduction product of the following compound with  $\text{NaBH}_4$  in methanol?



4) Which is the main reduction product of the following compound with  $\text{LiAlH}_4$  in ether followed by an aqueous workup?



5) The main product formed in the following reaction is,



### B. Answers in one sentence

- 1) What type of reducing agents are  $\text{NaBH}_4$  and  $\text{LiAlH}_4$ ?
- 2) Why  $\text{B}_2\text{H}_6$  acts differently than  $\text{NaBH}_4$  as a reducing agent.
- 3) Why alkali metals are using in Birch reduction?
- 4) What is the reagent used in Collins oxidation?
- 5) What is the reagent used in the Jones oxidation?
- 6) Write down the structure of DIBAL-H.
- 7) What is electron rich epoxidising reagent?
- 8) What is electron deficient epoxidising reagent?
- 9) What is the role of ammonia in the Birch reduction?
- 10) What is Mukaiyama aldol condensation reaction?
- 11) What is oxidation of Na, H and Boron in  $\text{NaBH}_4$ ?
- 12) What is oxidation of Li, H and Al in  $\text{LiAlH}_4$ ?
- 13) What is oxidative addition to any complex?
- 14) What is reductive elimination to any complex?
- 15) After addition of olefin what is the oxidation state of Rh in Wilkinson's catalyst?
- 16) In five coordinated species of Wilkinson's catalyst, how many total numbers of valance electrons are present?
- 17) What is sixth co-ordination site of Wilkinson's catalysts and total number of valance electrons?
- 18) What is hybridization of central metal ion and shape of Wilkinson's catalyst?
- 19) Is Wilkinson's catalyst homogeneous or heterogeneous?
- 20) Organ lithium and organ zinc, which is most reactive and why?
- 21) Write down the percentage of ionic character of organomagnesium, organozinc and organolithium.
- 22) What is Gilman's reagent?
- 23) Which is carbenoid reagent?
- 24) Which is most reactive reducing agent,  $\text{H}_2\text{-Pt/C}$ ,  $\text{H}_2\text{-Pd/C}$ ,  $\text{H}_2\text{-Ra-Ni}$ ?
- 25) What is the intermediate in Pinacol-Pinacolone rearrangement?
- 26) What are stabilized, non-stabilized ylides?

### C. Short notes

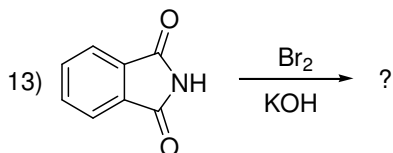
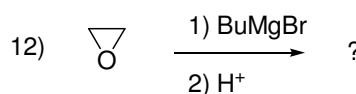
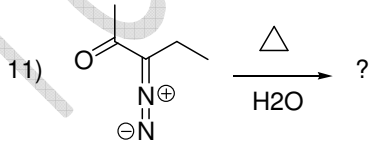
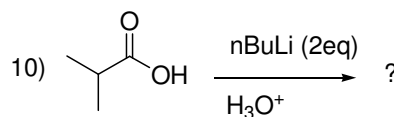
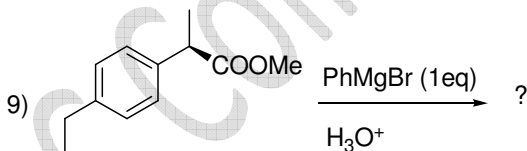
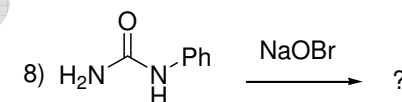
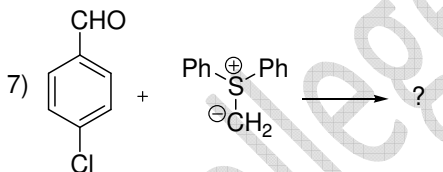
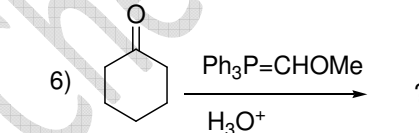
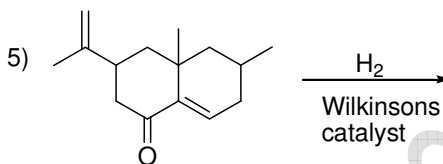
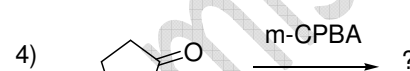
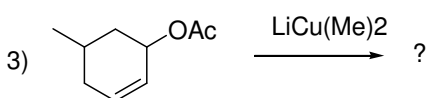
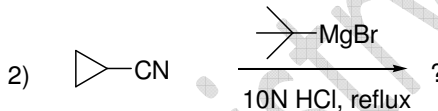
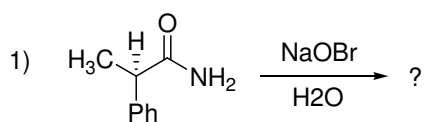
- 1) Ozonolysis
- 2) Favorskii rearrangement
- 3) Moffatt oxidation

- 4) Wolf-Kishner reduction
- 5) Simmons Smith reaction
- 6) Grignard reaction
- 7) Sommelet Hauser rearrangement
- 8) MPV reduction
- 9) Oppenauer oxidation
- 10) Cope rearrangement
- 11) Brook rearrangement
- 12) Benzidine rearrangement
- 13) Pummener rearrangement

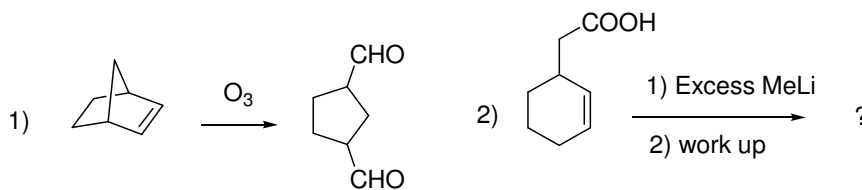
**D. Short answer questions.**

- 1) 4-t-butyl cyclohexanone on reaction with  $\text{NaBH}_4$  yields equatorial alcohol as the major product whereas tri-isobutyl lithium borohydride yields axial alcohol.
- 2) Esters with Grignard reagent give tertiary alcohol and amides give ketones.
- 3) Sulphur ylides could be used for synthesis of epoxide.
- 4) In catalytic reduction of nitriles to primary amines some secondary amines are also formed.
- 5) Wolff rearrangement is used to prepare higher homologue of starting acids.
- 6) Cyclohexane on treatment with  $\text{OsO}_4$  gives cis diol while peracid followed by hydrolysis gives trans diol.
- 7) 2-hydroxy acetophenone cannot be prepared by direct acylation of phenol but can be easily prepared by Fries rearrangement of phenyl acetate.
- 8) Organolithium reagents show 1, 2 addition to  $\alpha$ - $\beta$  unsaturated compounds while organocuprates shows 1,4 addition.
- 9) The compound  $(\text{CF}_3)(\text{Ph})(\text{OH})\text{C}-(\text{OH})(\text{Ph})(\text{CF}_3)$  is resistant to pinacol-pinacolone rearrangement.
- 10) Beckmann rearrangement is an antimigration type reaction. Explain with suitable examples.
- 11) Explain the role of peracid in epoxidation and lactonization reactions.
- 12) Give the significance of Reformatsky reaction.
- 13) What are P ylides and explain with suitable examples.
- 14) Explain Swern oxidation.
- 15) N-methyl benzamide does not undergo Beckmann rearrangement.
- 16) Trans-2-butene on reaction with  $\text{OsO}_4$  gives dl pair.
- 17) Stabilized P ylides are used for the synthesis of E alkene. Explain.
- 18) Phenyl lithium on reaction with  $\text{CO}_2$  followed by  $\text{H}_3\text{O}^+$  gives benzoic acid.
- 19)  $\beta$ -hydroxy ester could be synthesized by using organozinc compounds.
- 20) What is Swern oxidation? Give advantages of it giving suitable examples.
- 21) N-methyl phthalimide does not undergo Hoffman rearrangement to form N-methyl anthranilic acid.
- 22) Write the mechanism to convert alkene into alkanes using Wilkinson's catalyst.
- 23) P ylides form alkene while S ylides form epoxide when reacted with ketone carbonyl.

- 24) To synthesize  $\beta$  hydroxyl ester, Reformatsky reaction is preferred over Grignard reaction.
- 25) Explain stereochemistry and regiochemistry of organoboranes in organic synthesis giving suitable examples.
- 26) Cyclohexanone on Beckmann rearrangement gives  $\epsilon$ -caprolactam and under Bayer Vilsmeier oxidation gives  $\epsilon$ -lactone. Explain.
- 27) Hydroboration of 1-methyl cyclopentene followed by oxidation with  $\text{H}_2\text{O}_2/\text{NaOH}$  gives trans-2-methyl cyclopentanol.
- 28) In the Beckmann rearrangement of oxime having chiral carbon, retention of configuration is observed at the migrating carbon.
- 29) Predict the products with mechanism.

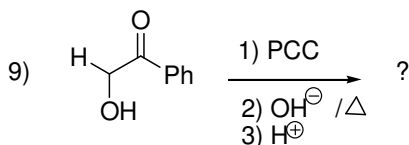
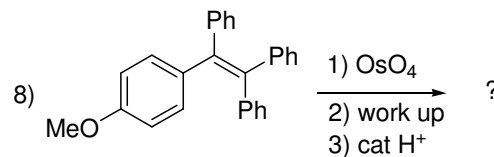
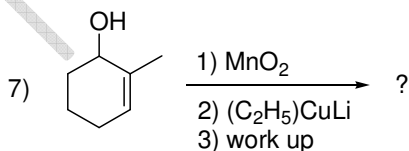
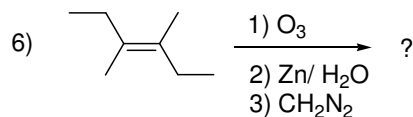
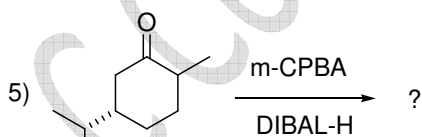
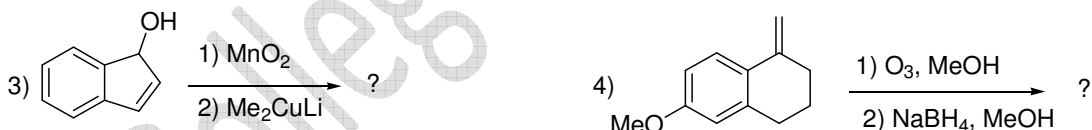
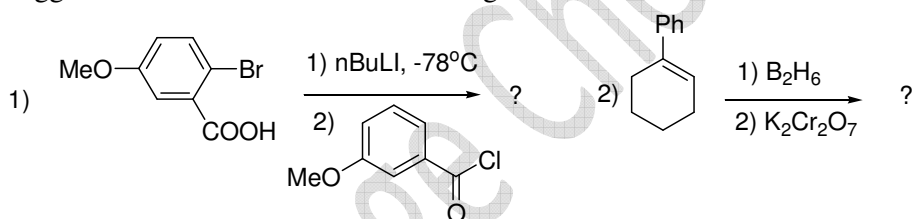


- 30) Suggest the mechanism for the following.

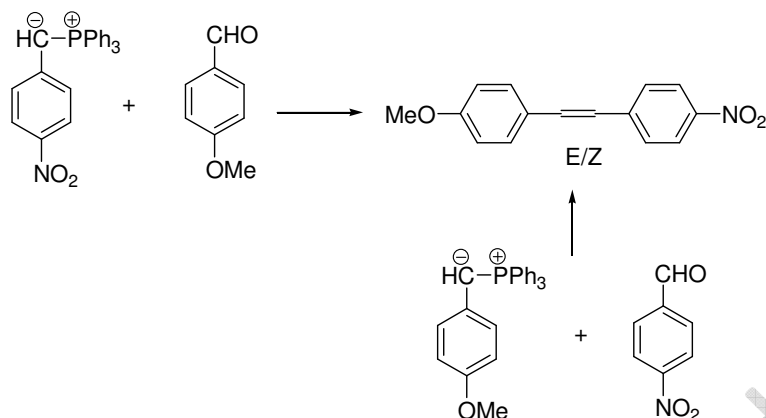


### E. Long answer questions

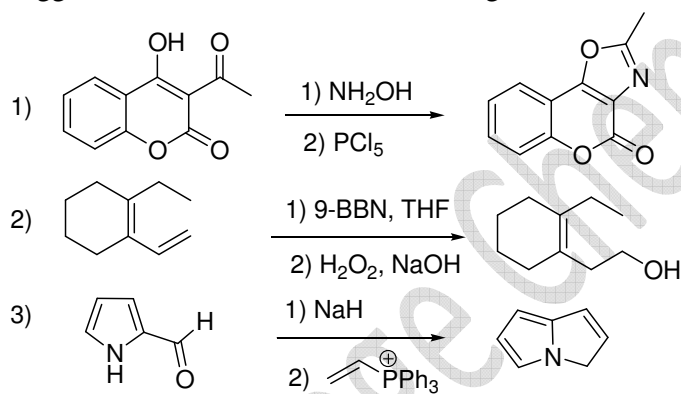
- 1) Explain the use of organozinc compounds in organic synthesis.
- 2) Explain with mechanism-Horner Wadsworth Emmons modification in Wittig reaction.
- 3) Discuss synthetic applications of Sulphur ylides.
- 4) Explain Organocopper reagents in organic synthesis.
- 5) Discuss the use of Phosphorous ylides in organic synthesis.
- 6) Discuss the use of  $\text{NaCNBH}_3$  in organic synthesis.
- 7) Discuss Birch reduction with examples.
- 8) Discuss the applications of  $\text{SeO}_2$  in organic synthesis
- 9) Discuss the synthetic applications of DIBAL-H
- 10) Explain the stereochemistry of Hydroboration reaction with suitable examples.
- 11) Explain the use of DDQ in organic synthesis with suitable examples.
- 12) Suggest the mechanism for the following.



13) Explain why the ratios of E:Z alkene in the product are different in the following reaction.



14) Suggest the mechanism for the following.



## Section II

### A. Objective questions

- What is the wavelength range for UV spectrum of light?
  - 400 nm to 700 nm
  - 700 nm to 1 mm
  - 0.01 nm to 10 nm
  - 10 nm to 400 nm
- The vibrations, without a center of symmetry are active in which of the following region?
  - Infrared but inactive in Raman
  - Raman but inactive in IR
  - Raman and IR
  - Inactive in both Raman and IR
- What is the order of decreasing vibrational frequency for C-Cl, C-Br, C-C, C-O and C-H?
  - C-H, C-C, C-O, C-Cl, C-Br
  - C-Cl, C-Br, C-C, C-H, C-O

- c) C-O, C-H, C-Br, C-Cl, C-C  
 d) C-Br, C-Cl, C-C, C-O, C-H

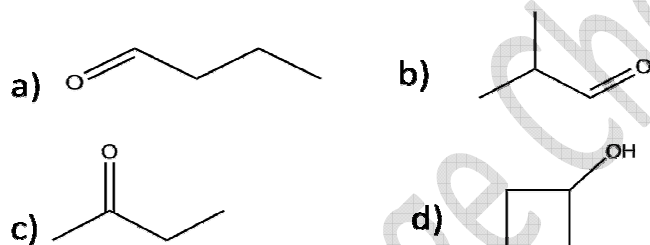
4) What is the correct increasing order of stretching frequencies for  $C \equiv C$ ,  $C = C$  and  $C - C$ ?

- a)  $C - C > C = C > C \equiv C$   
 b)  $C \equiv C > C = C > C - C$   
 c)  $C - C > C = C < C \equiv C$   
 d)  $C \equiv C < C - C > C = C$

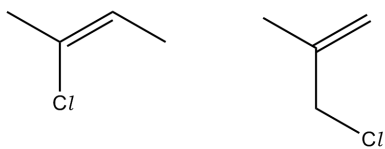
5) How many peaks would the carbon-13 NMR spectrum of the following compound show?

- a) 4    c) 8  
 b) 6    d) 9

6) Which molecule has four carbon environments, four proton environments and a characteristic proton NMR peak at  $\sim 9.5$  ppm?



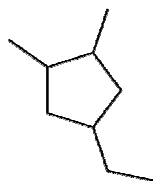
7) The two isomers shown could be very difficult to distinguish from each other with typical qualitative testing.



Which of the following instrumental techniques would be useful in distinguishing them from each other?

**1:** mass spectrometry **2:** carbon-<sup>13</sup> NMR **3:** proton NMR

- a) 1, 2 and 3



- b) only 1 and 2
- c) only 2 and 3
- d) only 1

**B. Answers in one sentence**

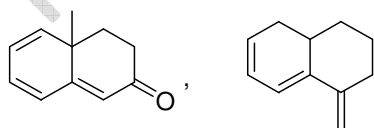
1. What are internal standards for  $^1\text{H}$  NMR?
2. Why TMS shows Singlet in  $^1\text{H}$  NMR?
3. Which are the solvent used in NMR?
4. What is the natural abundance of NMR active isotope of hydrogen?
5. What is the natural abundance of NMR active isotope of Carbon?
6. Why TMS is used as internal standard in NMR ?
7. What is the pattern of Mass spectra if compound contains two Bromine atom?
8. What do you mean by Molecular ion peak ?
9. What do you mean by Base peak?
10. What is the difference between EI mass spectra?
11. What is the long form of MALDI in mass spectroscopy?
12. Why is  $\text{CDCl}_3$  a triplet in  $^{13}\text{C}$  NMR?

**C. Short notes**

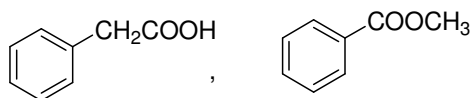
- 1) Diamagnetic Anisotropy
- 2) Chemical shift
- 3) McLafferty rearrangement
- 4) Nuclear Overhauser Effect
- 5) Proton coupled and proton decoupled spectra
- 6) DEPT in CMR
- 7) OFF resonance spectra
- 8) Double focusing mass spectrometer
- 9) Coupling constant
- 10) Write note on anisotropic effect.
- 11) Applications of IR spectroscopy?
- 12) Factors affecting chemical shift

**D. Short answer questions.**

- 1) Calculate  $\lambda_{\text{max}}$  of following compound

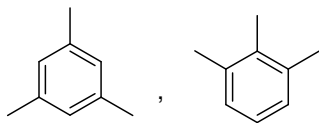


- 2) How you will distinguish following compound by IR spectroscopy?

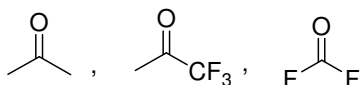


- 3) How you will distinguish following compound by PMR?

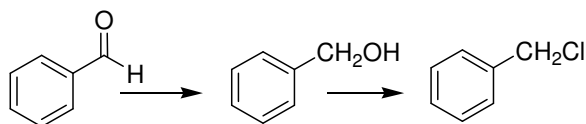




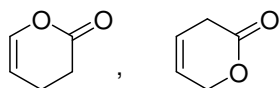
- 4) Assign the IR absorption values 1720, 1769, and 1928 cm<sup>-1</sup> to the following compounds with proper justification



- 5) How you will monitor the following conversions by IR?



- 6) Explain CDCl<sub>3</sub> is used as a solvent in CMR.  
 7) Aniline shows hypsochromic shift in acidic medium, explain.  
 8) Explain the term chromophore with example.  
 9) What is bathochromic shift, give example?  
 10) How you will distinguish following compound by IR spectroscopy?



- 15) Explain why <sup>13</sup>C NMR shows weak signals whereas <sup>1</sup>H NMR shows strong signals?  
 16) <sup>1</sup>H-NMR spectrum of acetonitrile shows shielded protons Explain.  
 17) Explain fundamental vibrations and overtones.  
 18) Explain CDCl<sub>3</sub> is used as solvent in CMR spectroscopy.  
 19) Explain the genesis of the following ions in the given compound.  
 CH<sub>3</sub>COCH<sub>3</sub>, 2-Propanol  
 20) How you will distinguish with the help of <sup>1</sup>H NMR?  
 21) How you will distinguish with help of FTIR?  
 22) How many peaks benzaldehyde shows in <sup>1</sup>H NMR?  
 23) Acetylene protons are deshielded whereas olefin protons are shielded. Explain.  
 24) How will you distinguish primary, secondary and tertiary alcohols by <sup>1</sup>H NMR Spectroscopy?  
 25) Assign the peaks of 4-methoxybenzaldehyde  
 26) Explain the peak at 2250 cm<sup>-1</sup> in IR?

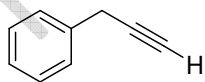
### E. Long answer questions.

- How will you distinguish 1°, 2° and 3° alcohols by <sup>1</sup>H NMR spectroscopy?
- Explain different factors affecting carbonyl IR stretching frequency
- Explain factors affecting chemical shift value in NMR.
- Deduce the structure from the following spectral data

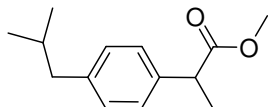
1. MF:  $C_{10}H_{12}O_2$   
IR:  $1740\text{cm}^{-1}$   
 $\lambda_{\text{max}}$ : 255nm  
PMR,  $\delta$  : 2.0(s,3H) ;2.8(t,2H);4.3(t,2H); 7.2(m,5H)
2. MF:  $C_7H_7NO_3$   
IR: 3600, 1520,1360 $\text{cm}^{-1}$   
 $\lambda_{\text{max}}$ : 265nm  
PMR,  $\delta$  : 7.6(m,18mm) ;8.15(dd,6mm J=2,7Hz);2.9(s,6mm,exch  $D_2O$ );  
5.0(s,12mm)
3. MF:  $C_9H_{12}O$   
 $\lambda_{\text{max}}$ : 255nm  
PMR,  $\delta$  : 1.15(3H,t J=7.5Hz) ;3.5(2H,q J=7.5Hz );4.4(2H,s); 7.2(5H,s)
4. MF:  $C_7H_{14}O_2$   
PMR,  $\delta$  : 0.9(d,6H) ;1.3(t,3H);2.4(q,2H); 1.9(m,1H): 3.9(m,1H)
5. MF:  $C_7H_{12}O_4$   
IR:  $1740\text{cm}^{-1}$   
PMR,  $\delta$  : 2.6(d,2H) ;1.3(d,6H J=6.5Hz );4.16(q,4H J=6.5Hz )
6. MF:  $C_4H_8O_2$   
CMR,  $\delta$  : 14.4(q) ;20.2(q); 60.4(t);170.7(s)
7. MF:  $C_6H_{10}O$   
CMR,  $\delta$  : 204(s) ;36(t, strong); 28(t, strong);24(t)
8. MF:  $C_8H_7OCl$   
PMR,  $\delta$  : 7.9(d,2H J=8Hz) ;7.3(d,2H J=8Hz);2.6(s,3H)  
CMR,  $\delta$  : 198(s) ;140(s);135(s);130(d): 129(d): 27(q)

5) Assign the CMR frequencies to following compound

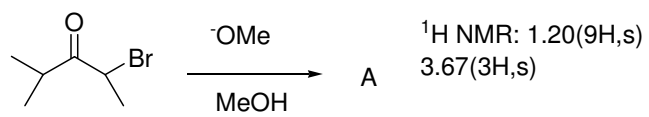
26.1(t), 138.9(s), 125.8(d), 128.7(d), 129.1(d), 70.9(d), 80.4(s)



6) Predict the  $^1\text{H}$  NMR chemical shift values to following compound



7) suggest the structure for A



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