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The Open University of Sri Lanka

B. Sc Degree / Stand Alone Programme 2008/2009

Organic Chemistry - CHU 3126 / CHE 5136

Level 5 - Assignment I - Test

Duration 1½ hours

Q	Marks	
	Max	Awarded
1	30	
2	20	
3	10	
4	30	
5	20	
Total		

Saturday 12<sup>th</sup> February 2009

Time: 4.00 – 5.30 p.m.

**Answer all questions.**

Maximum marks allocated to this paper are 110. However a candidate who scores 100 marks or above will be awarded 100% and those scoring less will be awarded the score they make.

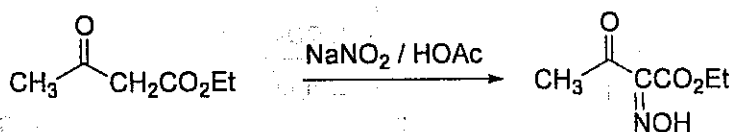
a. Draw resonance structures for pyridine



(ii). Giving reasons, explain which of the following is more basic, pyridine or piperidine.



(iii). During the synthesis of pyrroles, ethyl acetoacetate reacts with  $\text{NaNO}_2$  /  $\text{HOAc}$ . One of the primary reactions that take place is as follows.

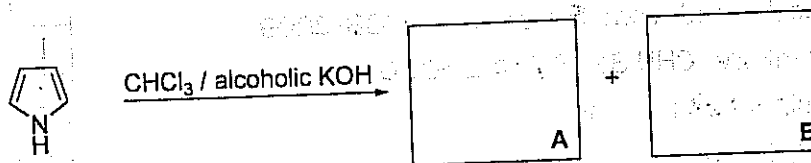
Give the mechanism of this reaction. (Hint:  $^+\text{NO}$  is formed from  $\text{NaNO}_2$  and  $\text{HOAc}$ ).

(30 Marks)

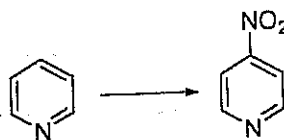
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2. (i) Identify the structures of the products A and B formed in the reaction given below.



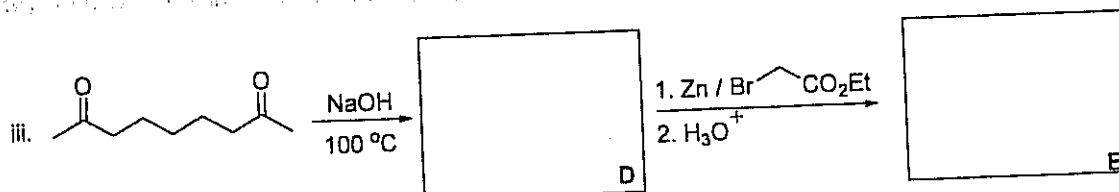
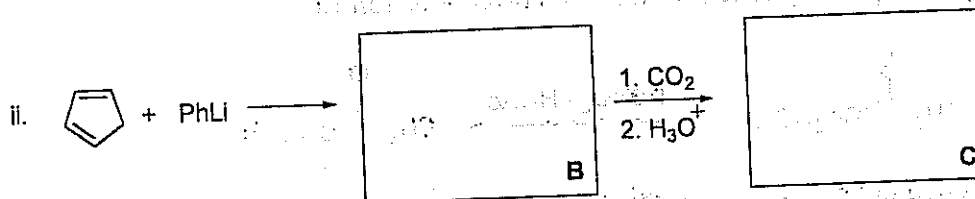
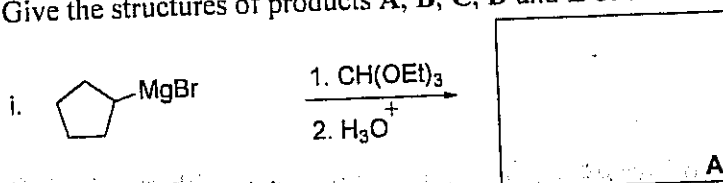
- (ii). Giving necessary reagents and conditions show how you would carry out the following conversions.



(20 Marks)

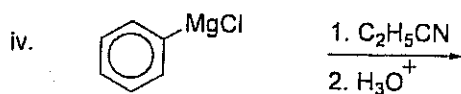
3. Give ONE example to illustrate nucleophilic substitution reaction of isoquinoline (10 Marks)

4. Give the structures of products A, B, C, D and E of the following reactions.



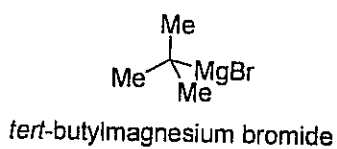
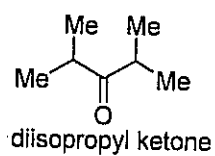
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(30 Marks)

5. Ketones with bulky groups do not undergo nucleophilic addition with Gignard reagents with bulky alkyl group.  
Giving appropriate mechanisms, predict what happens when diisopropyl ketone reacts with *tert*-butylmagnesium bromide.



(20 Marks)





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**Answer Guide**

1. a. Draw resonance structures for pyridine

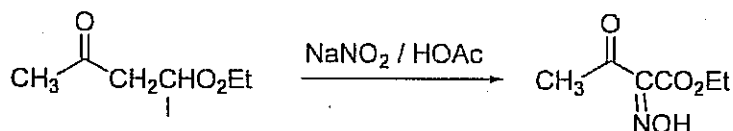


The answer is given in page 4 of your level 5 unit I book. Due to the electron withdrawing ability of N atom the ring becomes electron deficient and a positive charge delocalizes.

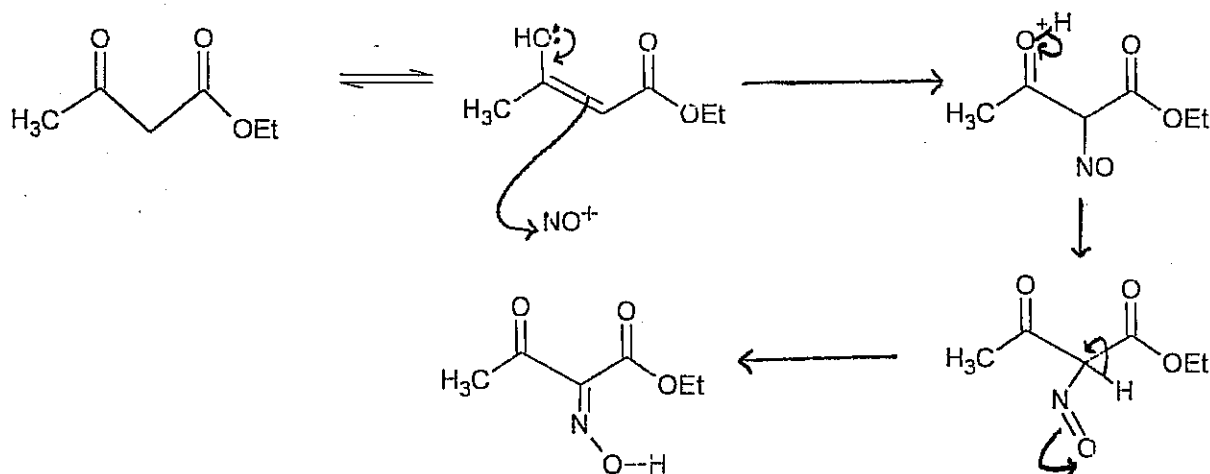
- (ii). Giving reasons, explain which of the following is more basic, pyridine or piperidine.

N atom of piperidine is  $sp^3$  hybridized. N atom of pyridine is  $sp^2$  hybridized. Lone pair electron of pyridine is in  $sp^2$  orbital. Lone pair electron of piperidine is in  $sp^3$  orbital. Donation of lone pair to a proton is difficult from  $sp^2$  orbital than from  $sp^3$  orbital. Therefore pyridine is less basic than piperidine.

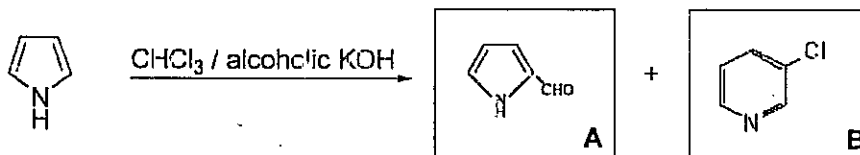
- (iii). During the synthesis of pyrroles, ethyl acetoacetate reacts with  $\text{NaNO}_2 / \text{HOAc}$ . One of the primary reactions that take place is as follows.



Give the mechanism of this reaction. (Hint:  $^+\text{NO}$  is formed from  $\text{NaNO}_2$  and  $\text{HOAc}$ )



2. (i) Identify the structures of the products A and B formed in the reaction given below.



The answer is given in page 30 of your level 5 unit I book.  
Reimer-Tiemann Reaction.

- (ii). Giving necessary reagents and conditions show how you would carry out the following conversions.

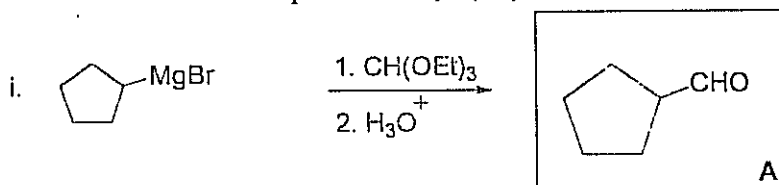


The answer is given in page 16 of your level 5 unit I book.  
Chemistry of pyridine-N-oxides.

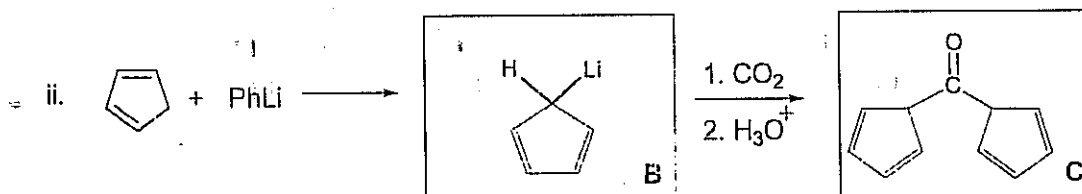
3. Give **ONE** example to illustrate nucleophilic substitution reaction of isoquinoline

The answer is in page 41 of your level 5 unit 1 book. Nucleophilic Substitution Reaction.

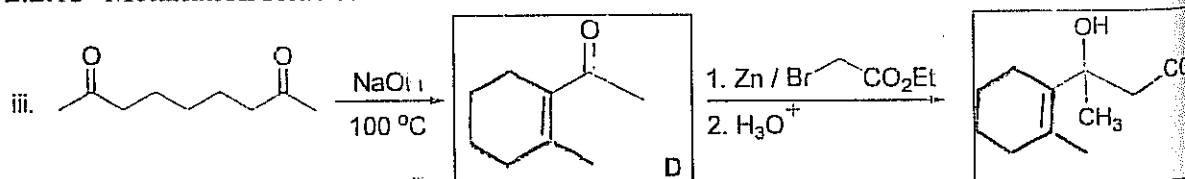
4. Give the structures of products **A**, **B**, **C**, **D** and **E** of the following reactions.



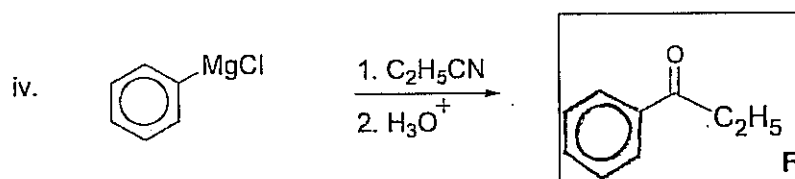
Ref: Unit II Synthetic organic Chemistry Part I Page No. 14  
1.4.4. Preparation of aldehydes



Ref: Unit II Synthetic Organic Chemistry Part I Page No. 21  
2.2.13- Metallation Reaction



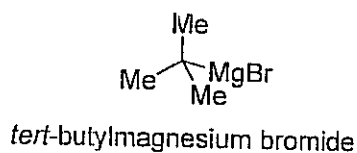
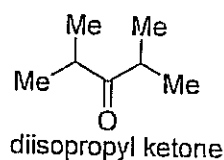
Ref: Unit II Synthetic Organic Chemistry Part I Page No. 30  
Reformatsky Reaction



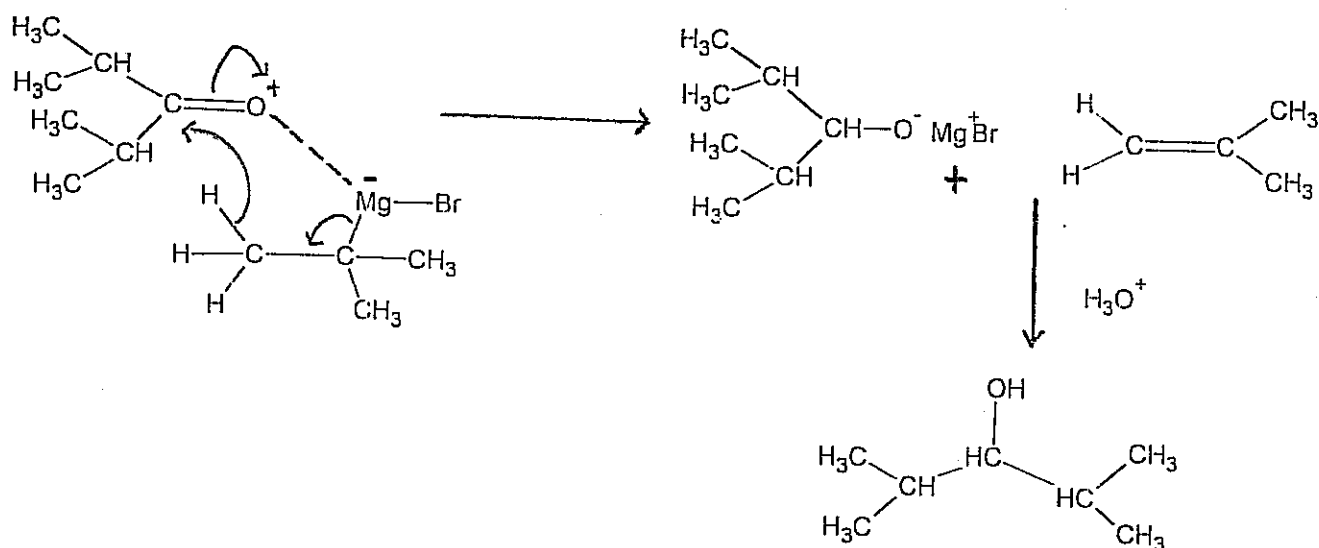
Ref: Unit II Synthetic Organic Chemistry Part I Page No. 15  
Preparation of ketones, alkyl nitriles with Grignard reagents.

5. Ketones with bulky groups do not undergo nucleophilic addition with Gignard reagents with bulky alkyl group.

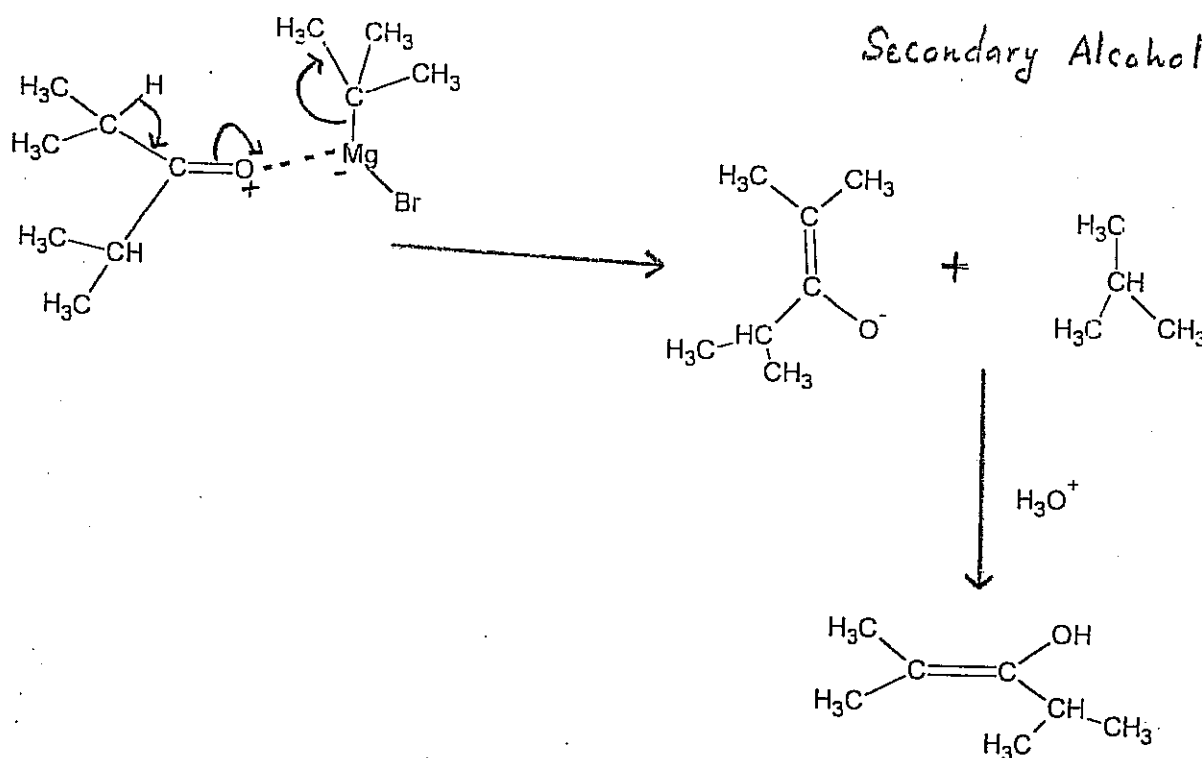
Giving appropriate mechanisms, predict what happens when diisopropyl ketone reacts with *tert*-butylmagnesium bromide.



Diisopropyl alcohol contains  $\alpha$  H; *tert* butyl magnesium bromide contains  $\beta$  H.



Secondary Alcohol 65%



Enolate 35%