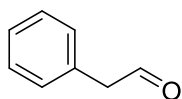
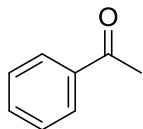


## Section A (answer 3 out of 5 questions; 15 min per question)

- (1) Give the products of the reaction compound **A** and **B** with the following reagents (i.e. **A-a**, **A-b**, **A-c** etc. and **B-a**, **B-b**, **B-c** etc.):



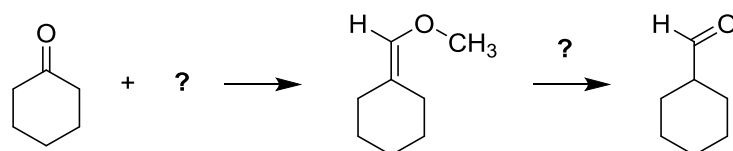
**A**



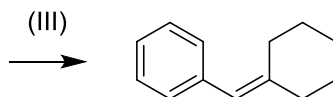
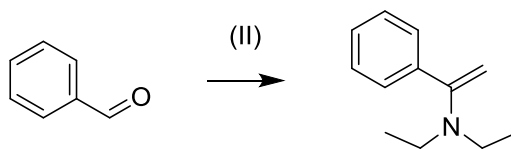
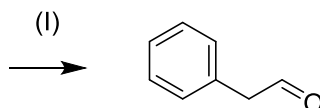
**B**

- (a)  $\text{NaBH}_4$ , then  $\text{H}_3\text{O}^+$  (b) Tollens' reagent  
 (c)  $\text{NH}_2\text{OH}$ , HCl catalyst (d)  $\text{CH}_3\text{MgBr}$ , then  $\text{H}_3\text{O}^+$   
 (e) 2  $\text{CH}_3\text{OH}$ , HCl catalyst (f)  $\text{H}_2\text{NNH}_2$ , KOH  
 (g)  $(\text{C}_6\text{H}_5)_3\text{P}=\text{CH}_2$  (h) HCN, KCN

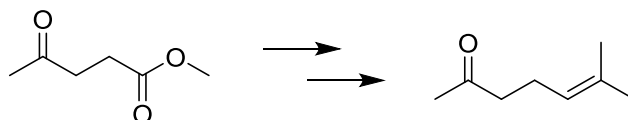
- (2) For the following reaction, suggest the missing reagents (labelled “?”) and propose a reaction mechanism.



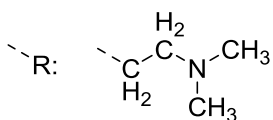
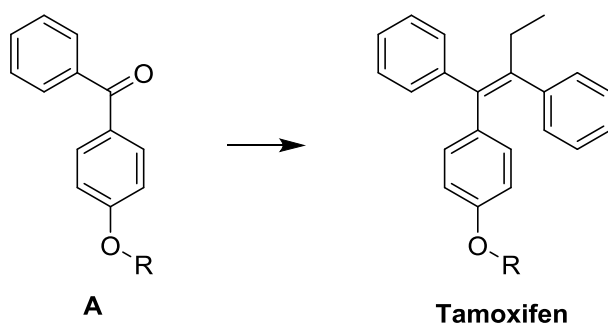
- (3) Propose reaction mechanisms and reagents for the following reactions I, II, and III.



- (4) Propose a reaction mechanism for the following reaction.

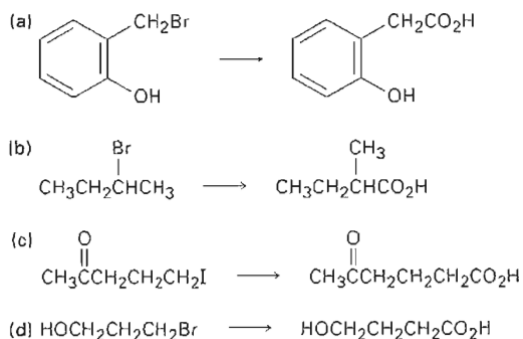


(5) How would you prepare Tamoxifen from compound **A** and benzene?

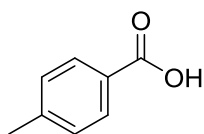


## Section B (answer 3 out of 5 questions; 15 min per question)

(6) Which method-Grignard carboxylation or nitrile hydrolysis-would you use for each of the following reactions? Explain.



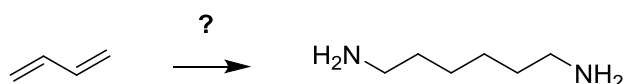
(7) Predict the product of the reaction of compound **A** with each of the following:



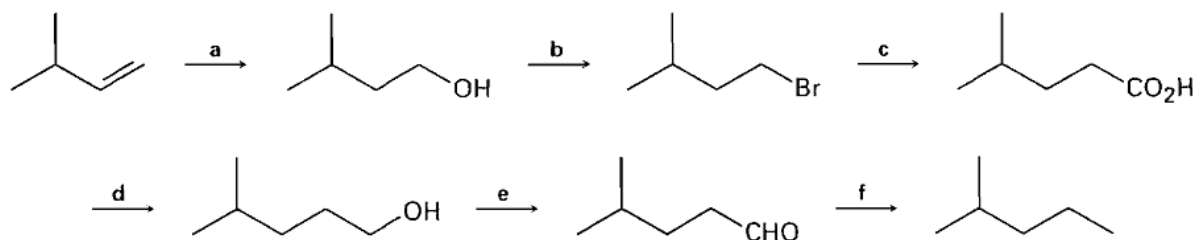
**A**

- (a)  $\text{LiAlH}_4$ , then  $\text{H}_3\text{O}^+$       (b) *N*-Bromosuccinimide in  $\text{CCl}_4$   
 (c)  $\text{CH}_3\text{MgBr}$  in ether, then  $\text{H}_3\text{O}^+$       (d)  $\text{KMnO}_4$ ,  $\text{H}_3\text{O}^+$

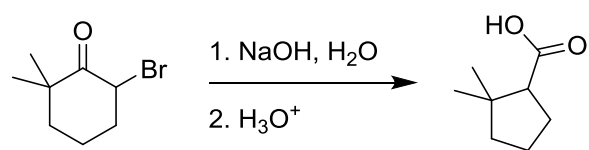
(8) Suggest a synthetic route for the following transformation:



(9) Identify the missing reagents in the following reaction scheme:

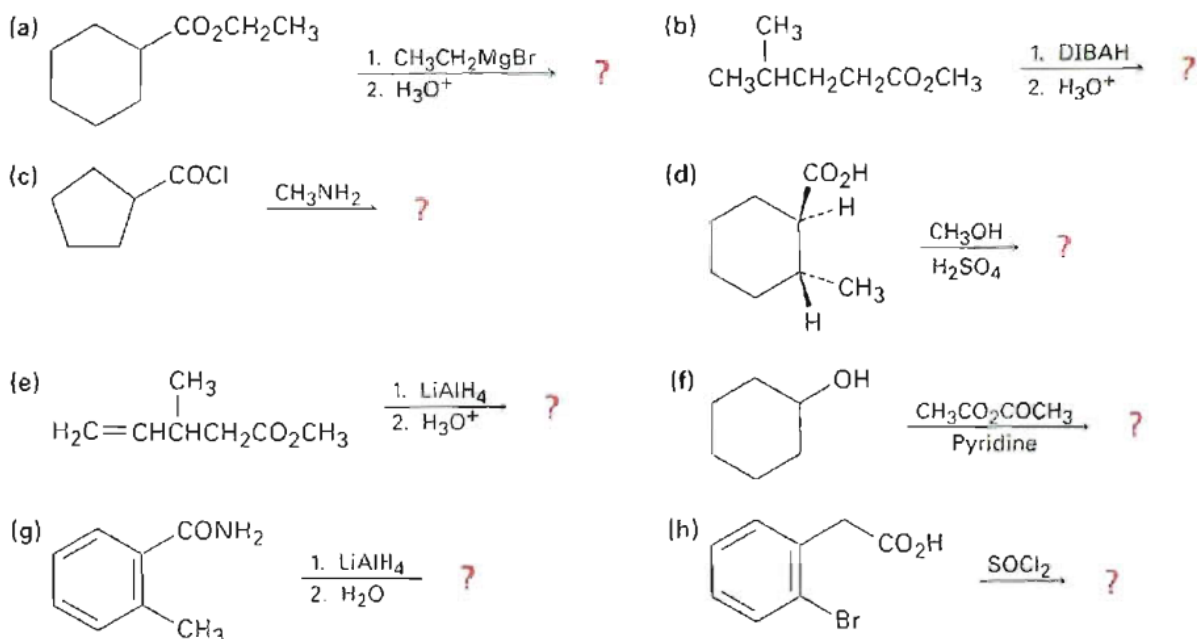


(10) Propose a mechanism for the following transformation:

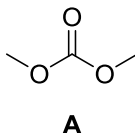


### Section C (answer 3 out of 5 questions; 15 min per question)

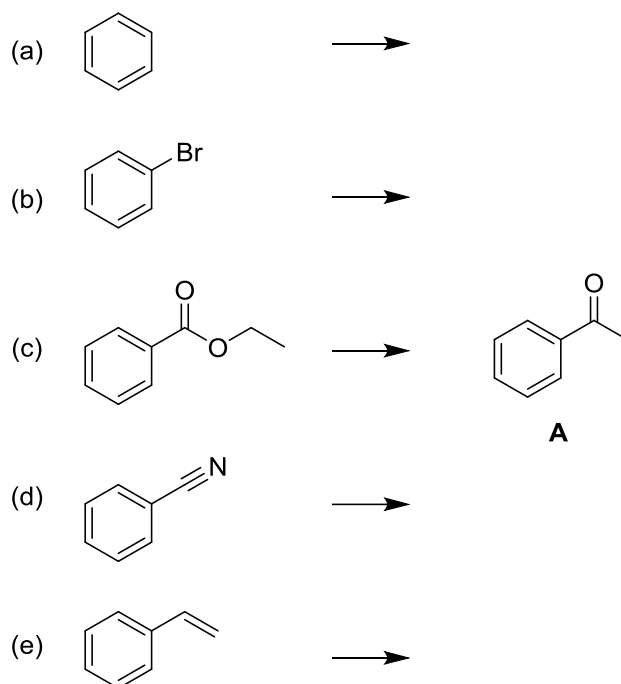
(11) Predict the product(s) of the following reactions:



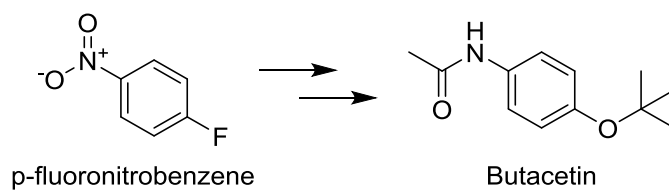
(12) Give the reaction mechanism and product from the Grignard reaction of an excess of compound **A** with phenylmagnesium bromide with compound **A**?



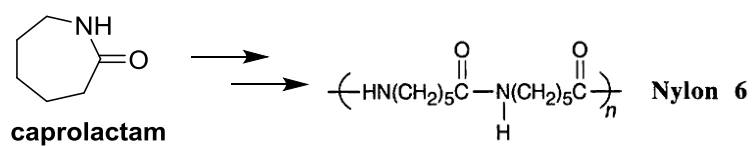
(13) Prepare compound **A** starting with compounds a-e (no mechanisms necessary).



(14) Suggest a synthetic route for Butacetin from p-fluoronitrobenzene.

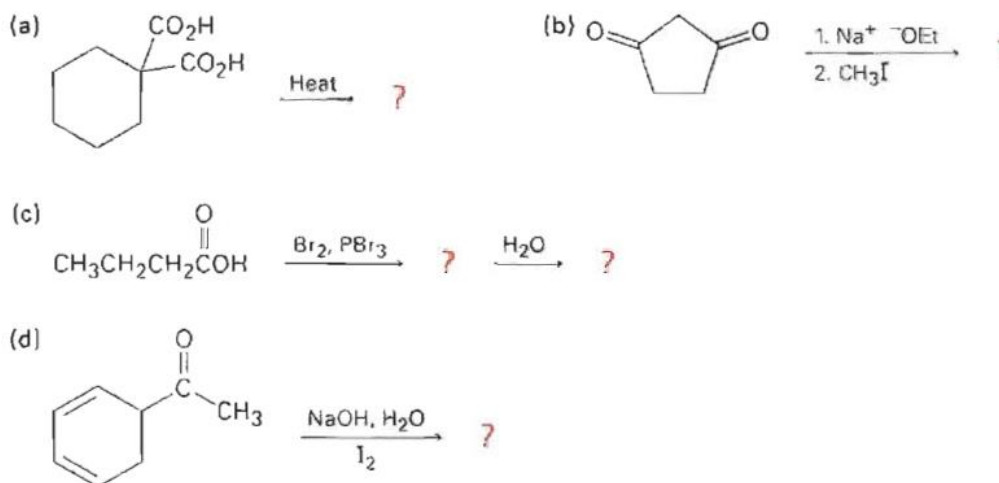


(15) Prepare nylon 6 starting with caprolactam (reaction mechanism).

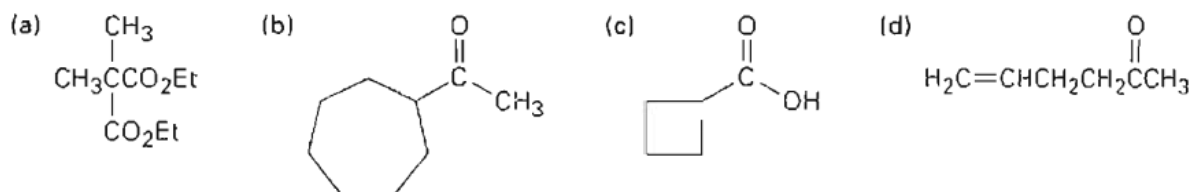


### Section D (answer 3 out of 5 questions; 15 min per question)

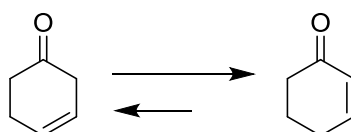
(16) Predict the product(s) of the following reactions:



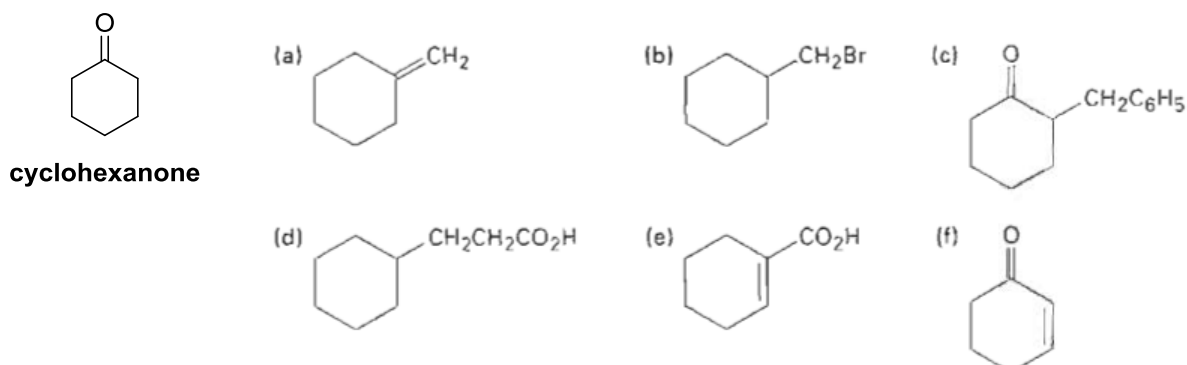
(17) How would you prepare the following compounds using either an acetoacetic ester synthesis or a malonic ester synthesis?



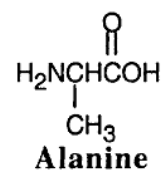
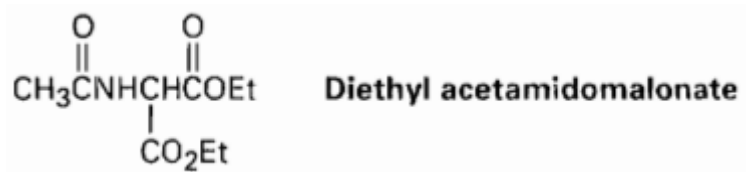
(18) Propose a mechanism for the following isomerisation under (a) acidic, and (b) basic conditions.



(19) How would you synthesize the following compounds from cyclohexanone?



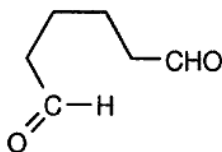
(20) Prepare alanine from diethyl acetamidomalonate.



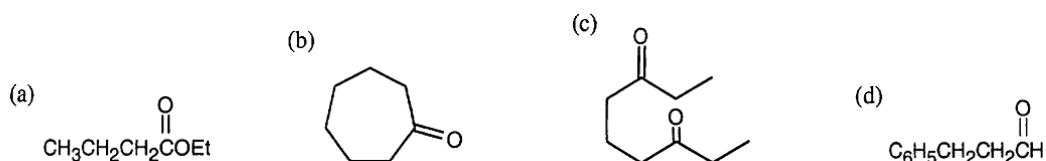


## Section E (answer 3 out of 5 questions; 15 min per question)

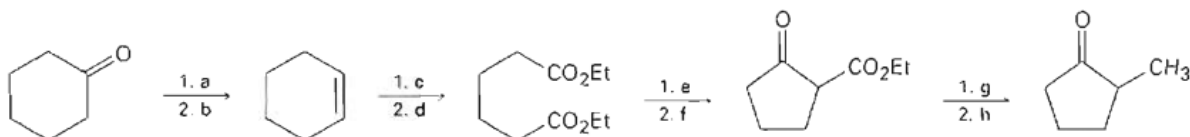
(21) What product would you expect to obtain from aldol cyclization of hexanedial?



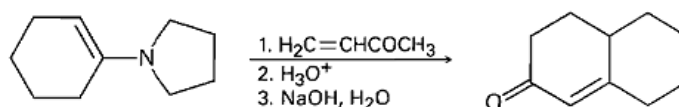
(22) What condensation products would you expect to obtain by treatment of the following substances with sodium ethoxide in ethanol?



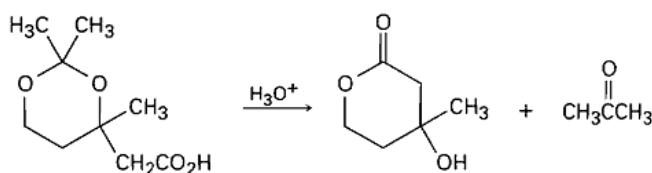
(23) Fill in the missing reagents a-h in the following scheme:



(24) The Stork enamine reaction and the intramolecular aldol reaction can be carried out in sequence to allow the synthesis of cyclohexenones. For example, reaction of the pyrrolidine enamine of cyclohexanone with 3-buten-2-one, followed by enamine hydrolysis and base treatment, yields the product indicated. Write each step, and show the mechanism of each.



(25) Show the mechanism for the following reaction:

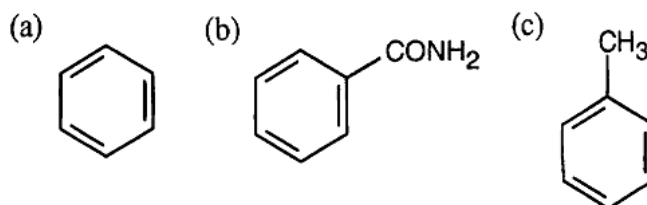


### Section F (answer 3 out of 5 questions; 15 min per question)

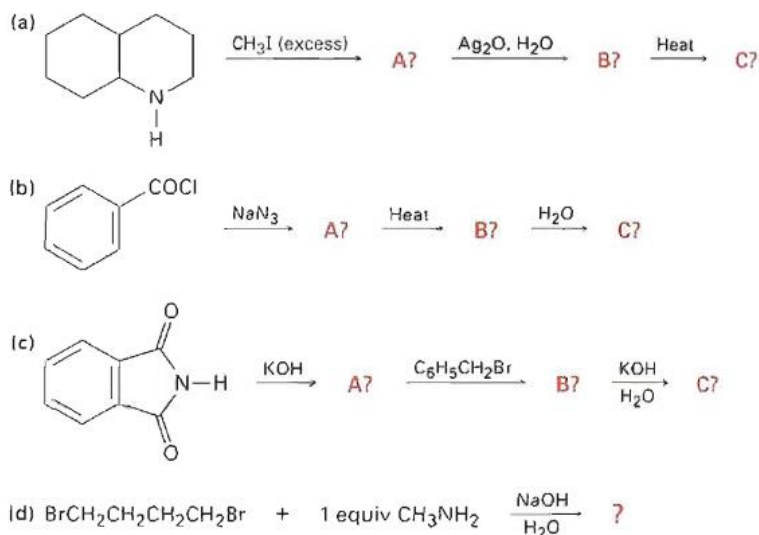
(26) How would you prepare the following compounds from 1-butanol:

- (a)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  **Butylamine**      (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  **Dibutylamine**      (c)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  **Propylamine**
- (d)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  **Pentylamine**      (e)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$  **N,N-Dimethylbutylamine**      (f)  $\text{CH}_3\text{CH}=\text{CH}_2$  **Propene**

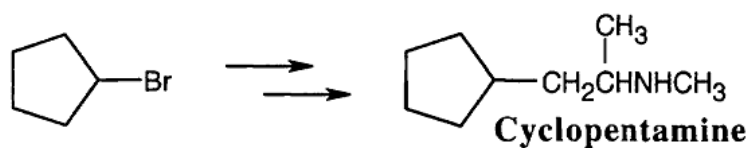
(27) How would you prepare aniline from the following compounds.



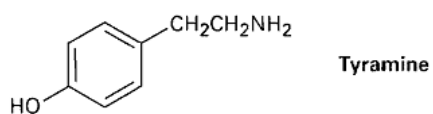
(28) Predict the product(s) from the following reactions. If more than one product is formed, tell which is the major.



(29) Cyclopentamine is an amphetamine-like central nervous system stimulant. Propose a synthesis of cyclopentamine starting with the following compound.

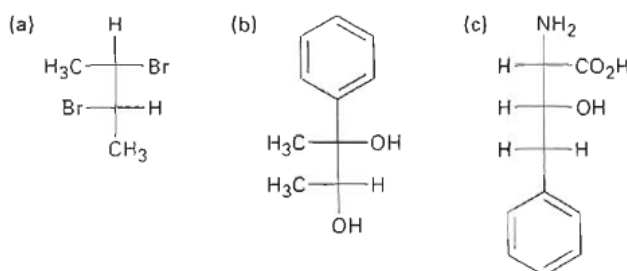


(30) Tyramine is an alkaloid found, among other places, in mistletoe and ripe cheese. How would you synthesize tyramine from benzene?



## Section G (answer 3 out of 5 questions; 15 min per question)

(31) Assign R or S configuration to each chirality center in the following molecules:

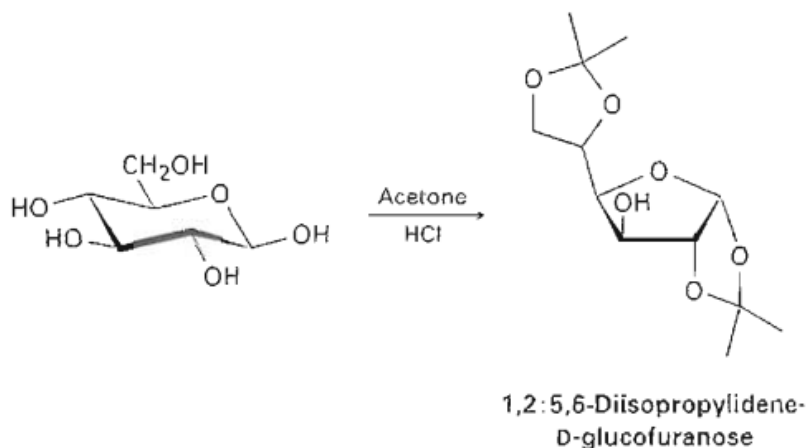


(32) Look up the structure of *n*-talose in Figure 25.3, and draw the  $\beta$  anomer in its pyranose form.

Identify the ring substituents as axial or equatorial. Draw structures for the products you would expect to obtain from reaction of  $\beta$ -D-talopyranose with each of the following reagents:

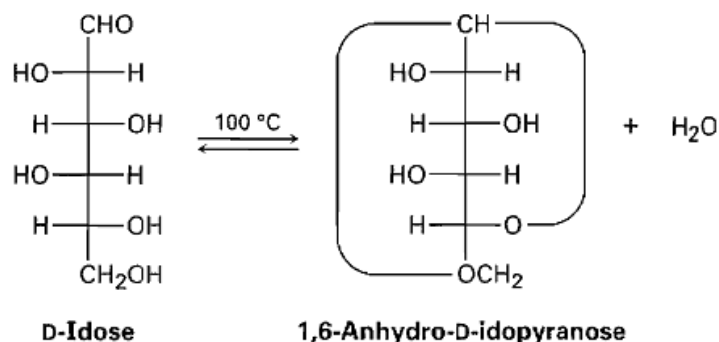
- (a)  $\text{NaBH}_4$  in  $\text{H}_2\text{O}$       (b) Warm dilute  $\text{HNO}_3$       (c)  $\text{Br}_2$ ,  $\text{H}_2\text{O}$   
 (d)  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{HCl}$       (e)  $\text{CH}_3\text{I}$ ,  $\text{Ag}_2\text{O}$       (f)  $(\text{CH}_3\text{CO})_2\text{O}$ , pyridine

(33) *n*-Glucose reacts with acetone in the presence of acid to yield the nonreducing 1,2:5,6-diisopropylidene-D-glucofuranose. Propose a mechanism.



(34) *n*-Mannose reacts with acetone to give a diisopropylidene derivative (Problem 33) that is still reducing toward Tollen's reagent. Propose a likely structure for this derivative.

(35) When heated to 100 °C, D-idose undergoes a reversible loss of water and exists primarily as 1,6-anhydro-D-idopyranose.



- Draw D-idose in its pyranose form, showing the more stable chair conformation of the ring.
- Which is more stable,  $\alpha$ -D-idopyranose or  $\beta$ -D-idopyranose? Explain.
- Draw 1,6-anhydro-D-idopyranose in its most stable conformation.
- When heated to 100 °C under the same conditions as those used for D-idose, D-glucose does not lose water and does not exist in a 1,6-anhydro form. Explain.