Name_____

Department of Chemistry and Biochemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #2 - March 14, 2005

ANSWERS

INSTRUCTIONS ---

This examination has two parts. Part I is in multiple choice format and the answers should be placed on the "Test Scoring Answer Sheet" which must be turned in and will be machine graded.

Part II requires your responding to questions by writing answers into the spaces provided in this booklet. This entire Exam Booklet must be handed in and will be returned to you with a grade. Write your name in the space above NOW.

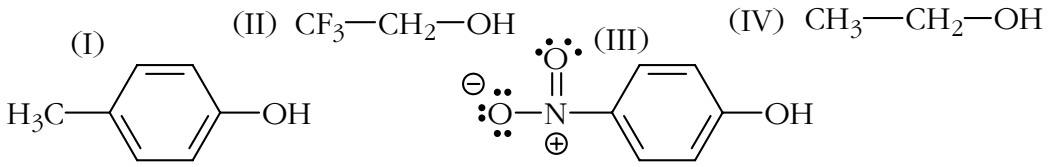
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places):
your name,
instructor's name,
your OSC student number, and
course number (30032201);
darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

You may use a set of molecular models but no other aids during the exam.

Answer all questions. The questions on Part I are worth 4 points each.

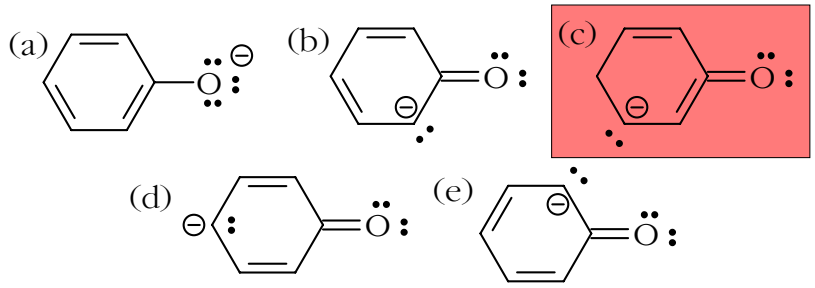
You have 50 minutes. Good luck!

1. Rank the following compounds in order of decreasing acidity (most acidic first).

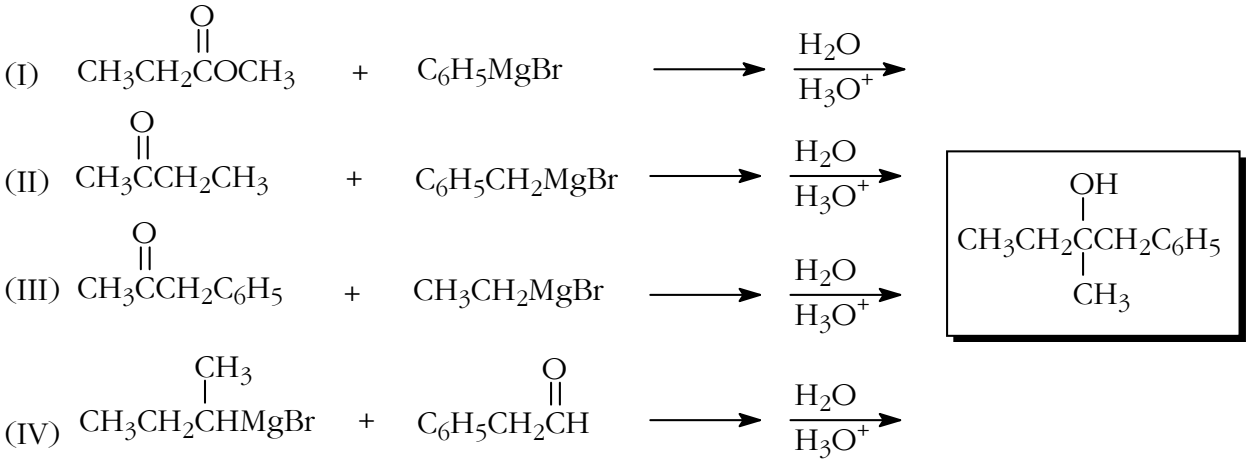


(a) I>II>III>IV, (b) I>III>IV>II, (c) III>I>II>IV, (d) IV>II>I>III
(e) None of the above answers is correct.
Phenols are more acidic than alcohols. Electron withdrawing groups increase acidity.

2. Which of the following resonance structures of the phenoxide anion is incorrect.

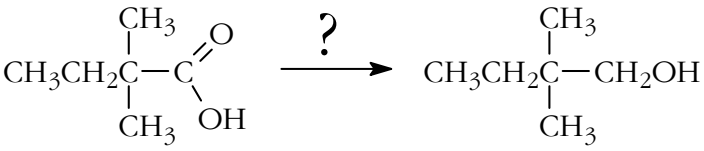


3. Which of the following procedures could be used to prepare 1-phenyl-2-methyl-2-butanol?



(a) I&II, (b) II&III, (c) III&IV, (d) I&III, (e) I&IV, (f) II&IV

4. What reagents would you use to bring about the following conversion?



(a) $LiAlH_4$ in ether, then H_3O^+/H_2O (b) CH_3MgBr, then H_3O^+/H_2O
(c) $NaBH_4$, then H_3O^+/H_2O (d) $KMnO_4/KOH$, then H_3O^+/H_2O
(e) Na, C_2H_5OH

5. Select the major product(s) of the following reaction.

$$CH_3CH_2OH + Na \longrightarrow$$

(a) $CH_3CH_2O^- Na^+ + H_2$ (b) $CH_3\overset{\overset{O}{\|}}{C}H + NaH$ (c) $Na^+ {}^-CH_2CH_2OH + H_2$

(d) $CH_3CH_2OCH_2CH_3 + NaOH + H_2$ (e) No reaction takes place.

6. Which product would be formed, after workup with dilute sulfuric acid, when an excess of phenylmagnesium bromide, Ph-Mg-Br, reacts with methyl benzoate, $PhCOOCH_3$?

(a) Ph_3C-OH, (b) Ph_2CH-OH, (c) Ph-CO-Ph, (d) Ph_3CH,
(e) Bogus query! Phenylmagnesium does not react with esters.

7. Which of the following procedures could be used to prepare a secondary (2^o) alcohol?

I: Reduction of an aldehyde. II: Reduction of a ketone. III: Reduction of a carboxylic acid. IV: A Grignard synthesis using formaldehyde. V: A Grignard synthesis using an aldehyde other than formaldehyde. VI: A Grignard synthesis using a ketone.

(a) I, III, V, (b) II, IV, V, VI, (c) II, V, (d) I, II, III,
(e) None of the above answers is correct.

8. Which of the following functional groups cannot be present in a halogen-containing compound you wish to react with magnesium to form a Grignard reagent?

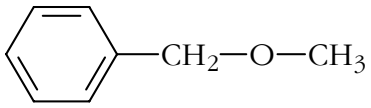
I: -COOH, II: $-COCH_3$, III: $-NO_2$

(a) I, (b) II, (c) III, (d) I&II, (e) I&III, (f) II&III, (g) I - III,
(h) Yo! Bogus question! Any of those three groups could be present.

9. Which of the following reagents would be most successful at converting 1-butanol to butanal, $CH_3CH_2CH_2CH{=}O$?

(a) $KMnO_4$, (b) CrO_3/H_2SO_4, (c) Na_2CrO_4/H_2SO_4, (d) $C_5H_6NCrO_3Cl/CH_2Cl_2$

10. A correct name for the compound on the right would be



(a) methyl phenyl ether. (b) benzyl methyl ether.
(c) dimethyl phenyl ether.
(d) methoxybenzene. (e) anisole.

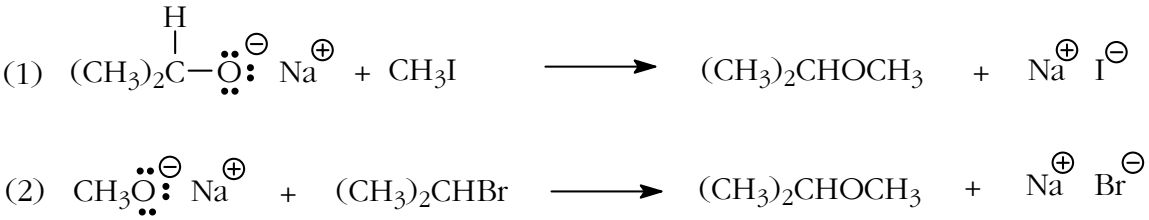
11. When *t*-butyl methyl ether is prepared by the bimolecular dehydration of ethanol,

$$(CH_3)_3COH + CH_3OH \xrightarrow{H_2SO_4} (CH_3)_3COCH_3 + H_2O ,$$

the reaction takes place, at least in part, *via*

(a) an S_N1 reaction; then methyl carbocation reacts with a molecule of *t*-butanol.
(b) an S_N1 reaction; then *t*-butyl carbocation reacts with a molecule of methanol.
(c) an S_N2 reaction of a methanol molecule with a protonated t-butanol.
(d) an S_N2 reaction of a t-butoxide anion with a protonated methanol.
(e) an S_N2 reaction of a methoxide anion with a protonated *t*-butanol.
(f) an E2 reaction between a methoxide anion and a *t*-butanol molecule.

12. Which synthesis of isopropyl methyl ether would give the better yield?

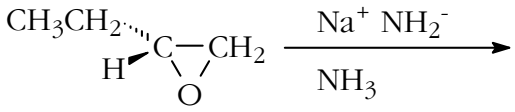


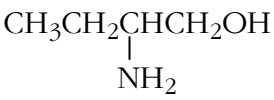
(a) 1, (b) 2, (c) 1 and 2 would give about the same yield,
(d) neither reaction would work, (e) What's a yield?

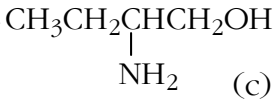
13. Rank the halogen acids in order of decreasing ability to cleave an ether (most reactive first).

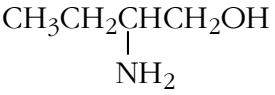
(a) HCl > HBr > HI, (b) HCl > HI > HBr, (c) HBr > HCl > HI, (d) HBr > HI > HCl,
(e) HI > HBr > HCl, (f) HI > HCl > HBr

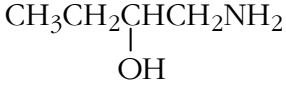
14. Predict the major product(s) in the following reaction.

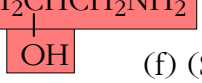


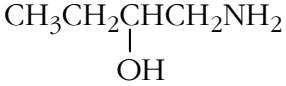
(a) racemic 

(b) (R)- 

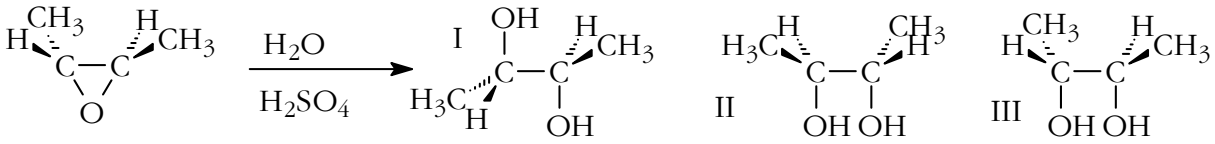
(c) (S)- 

(d) racemic 

(e) (R)- 

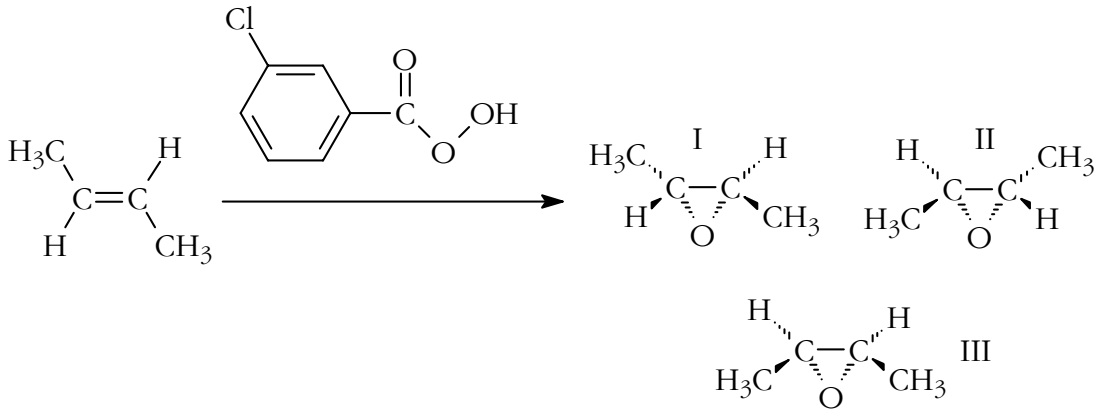
(f) (S)- 

15. Predict the major product(s) in the following reaction.



(a) I, (b) II, (c) III,
(d) II & III in unequal amounts, (e) II & III in equal amounts,
(f) I, II and III with II & III in unequal amounts,
(g) I, II and III with II & III in equal amounts

16. Predict the major product(s) in the following reaction.

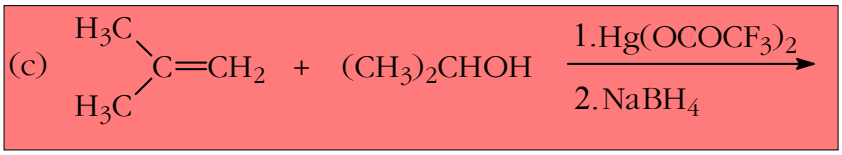


(a) I & II in equal amounts, (b) III, (c) I & II in equal amounts and III,
(d) None of the products shown would be major.

17. Which synthesis would you chose to make *t*-butyl isopropyl ether, $(CH_3)_3C\text{-}O\text{-}CH(CH_3)_2$, in the highest yield?

(a) $(CH_3)_3CO^- K^+ + (CH_3)_2CHBr \longrightarrow$

(b) $(CH_3)_3CBr + (CH_3)_2CHO^- Na^+ \longrightarrow$

(c) 

(d) Bogus question, dude! All of these reactions would produce the product in good yield.

18. Which of the following is not a property of diethyl ether?

(a) It forms explosive peroxides on long exposure to air.
(b) It is very flammable.
(c) It is only slightly soluble in water.
(d) It is oxidized to two molecules of acetic acid by potassium dichromate.

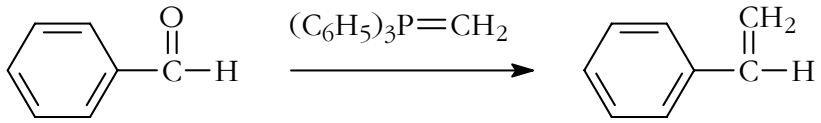
19. $CH_3COC_2H_5$ is an example of a(n)

(a) ether, (b) acid anhydride, (c) carboxylic acid, (d) ketone, (e) ester

20. Aldehydes and ketones typically undergo nucleophilic addition as opposed to nucleophilic substitution, which is a reaction type typical of carboxylic acid derivatives (acid chlorides, esters, *etc.*). Why do aldehydes not undergo nucleophilic substitution?

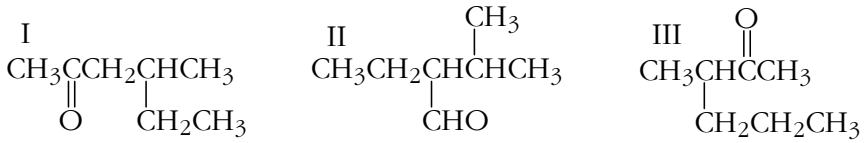
(a) Actually, they do; the question is bogus. (b) R^- and H^- are very poor leaving groups.
(c) R^- and H^- are very good leaving groups. (d) The carbonyl group is more polarized in the carboxylic acid derivatives.

21. The reaction shown below is an example of the _____.



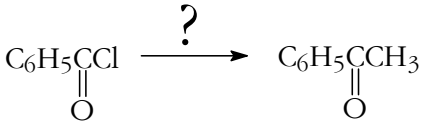
(a) Wolff-Kishner reaction, (b) Clemmensen reduction, (c) Hunsdiecker reaction, (d) Diels-Alder reaction, (e) Wittig reaction

22. Which of the compounds shown below are correctly named as butane derivatives, either as butanals or butanones?



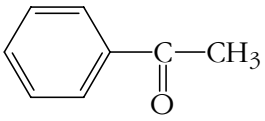
(a) I, (b) II, (c) III, (d) I&III, (e) None of them.

23. Which reagents would you use to bring about the conversion shown to the right?



(a) CH_3MgBr, ether, -78°, then dil. HCl,
(b) CH_3Li, ether, -78°, then dil. HCl,
(c) CH_3Br, $AlCl_3$,
(d) $(CH_3)_2CuLi$, ether, -78°,
(e) CH_3OH, H_3O^+, catalyst

24. The compound shown to the right is used as an artificial flavor in pistachio ice cream. Your boss, the president of Popular Pistachio Popsicle Products, asks you for suggestions as to how it could be made. If you want to retain your job, you could suggest simple syntheses (involving one or two closely related steps) using which of the following reactions?



(I) Friedel-Crafts acylation, (II) oxidation of a secondary alcohol, (III) reduction of a carboxylic acid, (IV) Wittig reaction

(a) I & II, (b) I & III, (c) I & IV, (d) II & III, (e) II & IV, (f) III & IV

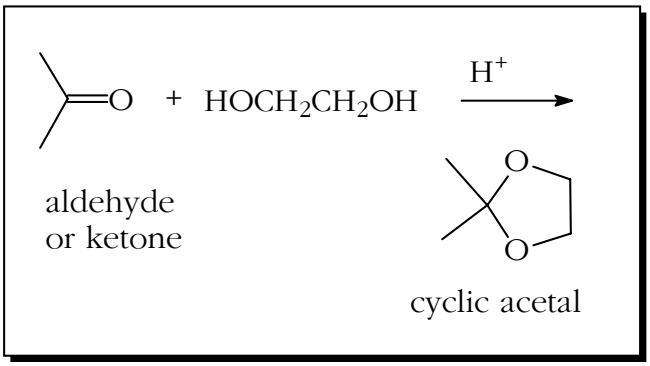
25. Aldehydes differ from ketones in that they
(I) are less reactive than ketones toward nucleophilic addition reactions.
(II) are more reactive than ketones toward nucleophilic addition reactions.
(III) are less easily oxidized than ketones.
(IV) are more easily oxidized than ketones.

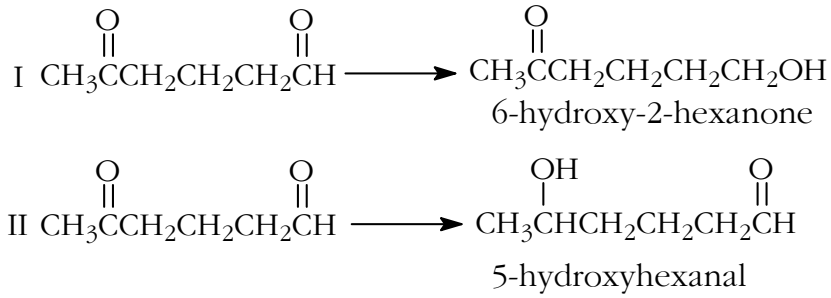
(a) I&III, (b) I&IV, (c) II&III, (d) II&IV,
(e) None of the above answers is correct.

26. Typical reactions of aldehydes and ketones involve attack of a(n) **A** reagent at the **B** atom of the carbonyl group.

(a) **A** = nucleophilic, **B** = oxygen, (b) **A** = nucleophilic, **B** = carbon,
(c) **A** = electrophilic, **B** = carbon, (d) **A** = radical, **B** = oxygen,
(e) Bogus question. Neither aldehydes nor ketones undergo any reactions.

27. Cyclic acetals of the sort shown in the box are frequently prepared during the course of a synthetic sequence for the purpose of "protecting" a carbonyl group. As Chief Chemist for the Cool Carbonyl Chemicals Corporation (Popular Pistachio went bankrupt), you have been assigned the task of making 6-hydroxy-2-hexanone and 5-hydroxyhexanal from 5-oxohexanal. Which, if either, of these syntheses will likely require the use of the acetal protecting group?



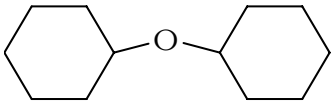


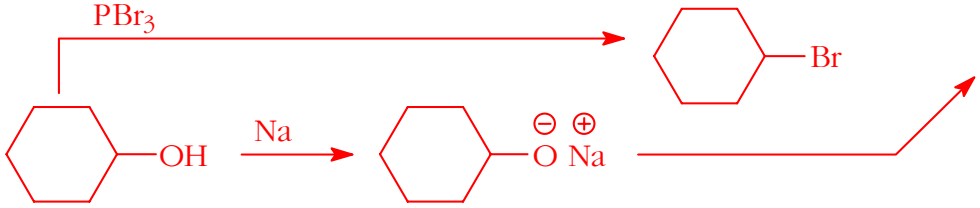
(a) Neither, (b) I, (c) II, (d) both

Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this.

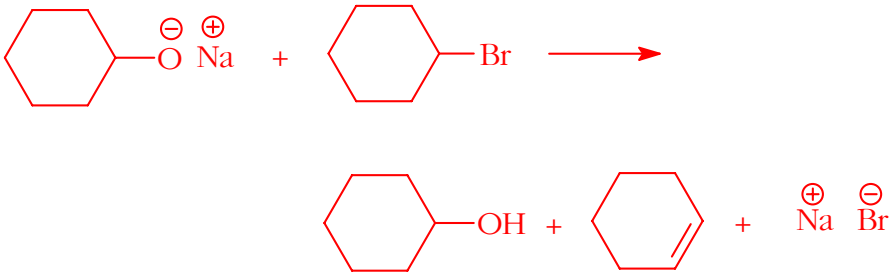
1. Synthesis. Draw an outline for the following syntheses. Show all materials and any special conditions employed as you write the reactions which constitute your outline. Do not balance equations or show mechanisms.

(a) Prepare dicyclohexyl ether using a Williamson synthesis. Available starting materials are alcohols containing up to 6 carbons and any needed inorganic materials.



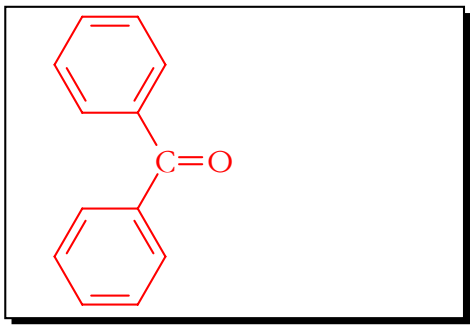


(b) The Williamson synthesis is not ideal for making the above compound. Write down the reaction that will lead to a significant amount of byproduct in this synthesis.



2. It's roadmap time! Based on the information provided, draw the structures of compounds A through D in the boxes provided.

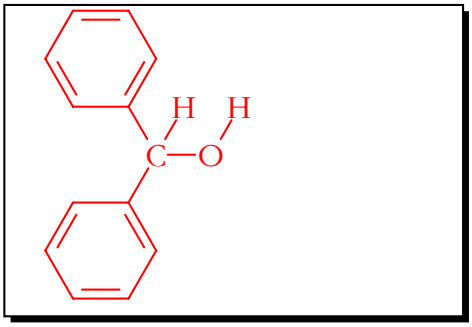
Compound A, $C_{13}H_{10}O$, has 5 signals in the C-13 NMR. When dissolved in alcohol and reacted with hydroxylamine it forms an oxime. It reacts with sodium borohydride to form compound B, $C_{13}H_{12}O$. Compound B reacts with phosphorous tribromide to give compound C, $C_{13}H_{11}Br$. Compound C reacts with triphenylphosphine, followed by sodium hydride, to give compound D, $C_{31}H_{25}P$. Compound D reacts with compound A to give tetraphenylethene. [Note: In the roadmap below, Ph represents the phenyl group.]



Compound A, $C_{13}H_{10}O$

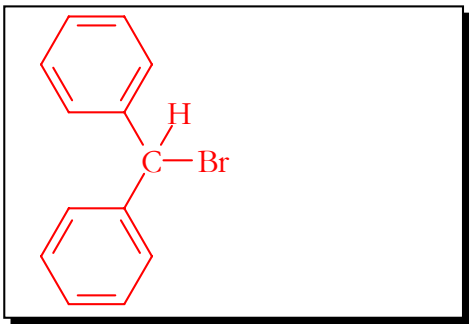
1) $NaBH_4$

2) H_2O, H_3O^+



Compound B, $C_{13}H_{12}O$

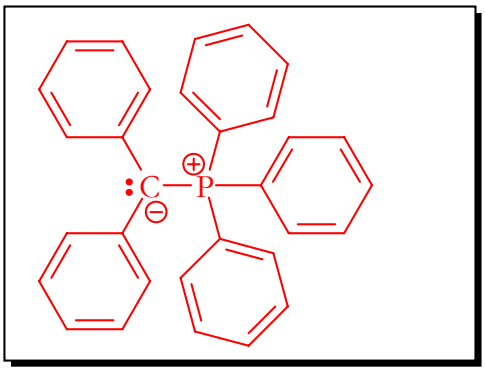
PBr_3



Compound C, $C_{13}H_{11}Br$

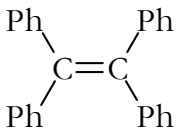
1) Ph_3P

2) NaH



Compound D, $C_{31}H_{25}P$

Compound A



Part I (108)	_____
Part II	
1. (9)	_____
2. (8)	_____
Total(125)	_____