

Name _____

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #1 - February 10, 2003

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 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 (or Social Security) number, course number (30032201) and the test number (01); darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles. (If you use your OSC Student number, enter the whole number including the prefix letter but do not darken any bubbles under the letter.)

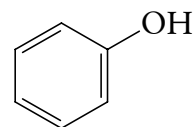
You may use a set of molecular models but no other aids during the exam.

Answer all questions. The questions on Part I are worth 2 points each.

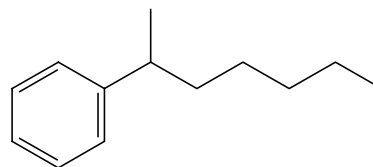
You have 90 minutes. Good luck!

1. Which of the following would be the best natural source of aromatic compounds?
 (a) petroleum, (b) bituminous coal, (c) anthracite coal, (d) natural gas
2. In chemical terms, an aromatic compound is one that
 (a) smells sweet. (b) smells putrid. (c) has a pleasant smell. (d) smells.
 (e) has chemical properties similar to those of benzene.
3. Which of the following series of numbers represents the number of π -electrons that could be found delocalized in conjugated monocyclic rings that are aromatic?
 (a) 2, 4, 6, 8, ...; (b) 3, 5, 7, 9, ...; (c) 4, 8, 12, 16, ...; (d) 2, 6, 10, 14, ...

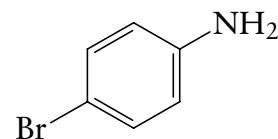
4. The compound shown to the right is known as



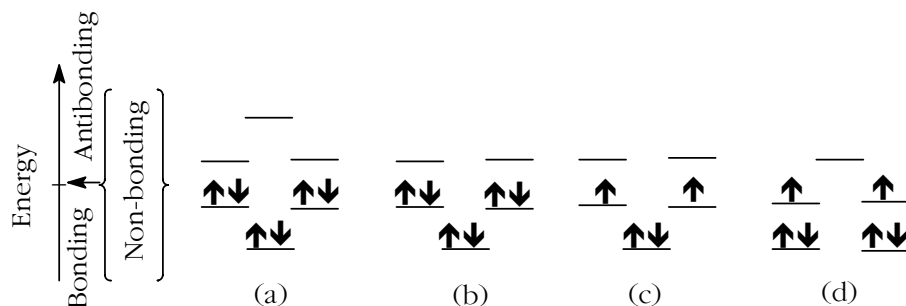
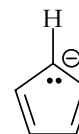
- (a) toluene, (b) phenol, (c) aniline, (d) phenyl, (e) styrene
5. The IUPAC name for the compound shown to the right is



- (a) 2-benzylheptane. (b) 2-phenylheptane.
 (c) 2-heptylbenzene. (d) 1-methyl-1-phenylhexane.
 (e) 1-methyl-1-benzylhexane.
6. A correct name for the compound shown to the right is

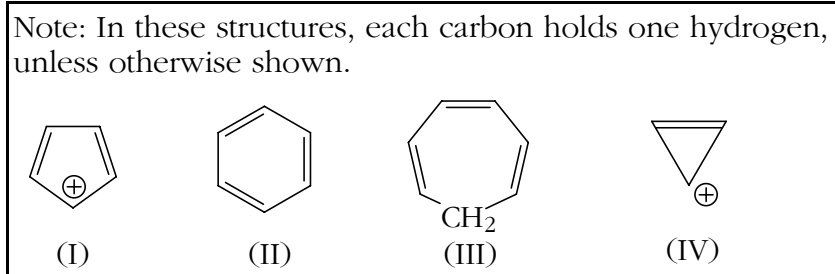


- (a) *p*-bromophenol. (b) 3-bromoaniline.
 (c) *p*-bromoaniline. (d) 4-bromoanthracene.
 (e) None of the above names is correct.
7. Which of the following is the best representation of the π molecular orbitals in the cyclopentadienide anion, $C_5H_5^{-1}$?

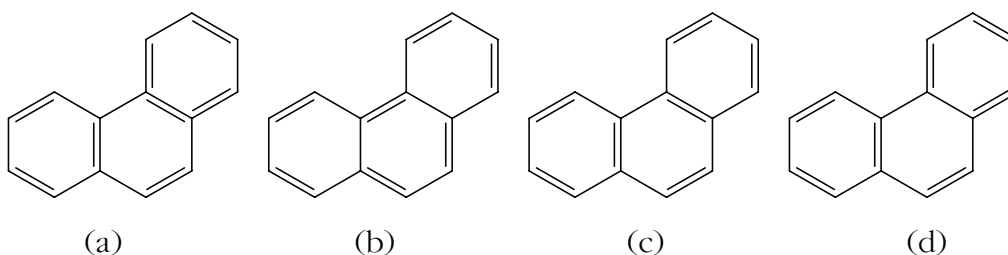


- (d) None of the above answers is correct.

8. Which of the following rings should *not* be aromatic?



- (a) I & II, (b) II & III, (c) III & IV, (d) I & III, (e) II & IV,
 (f) None of the above answers is correct.
9. Which of the following is *not* a valid resonance structure for phenanthrene?

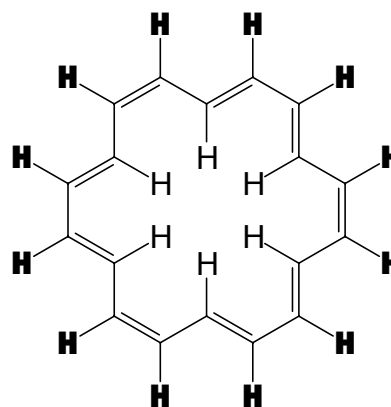


10. Benzene is most prone to undergo which of the following?

(a) electrophilic addition, (b) nucleophilic addition,
 (c) electrophilic substitution, (d) nucleophilic substitution

11. In the proton NMR spectrum of [18]annulene, the structure of which is shown to the right, the interior hydrogens (H) appear at -3.0 ppm (upfield) from TMS, while the exterior hydrogens (H) appear at 9.3 ppm (downfield) from TMS. This difference in chemical shift can be explained in terms of

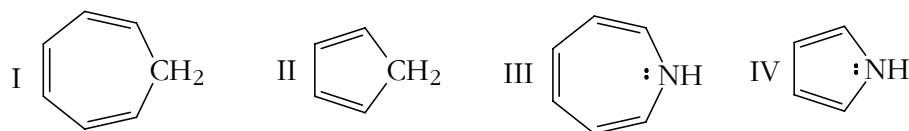
(a) a steric factor.
 (b) different hybridization of the carbons holding the two different types of hydrogen.
 (c) the interior hydrogens being attached to *trans* double bonds.
 (d) a ring current around the aromatic system.



12. The idea that real benzene is about 150 kJ/mol (36 kcal/mol) more stable than the *hypothetical* 1,3,5-cyclohexatriene (which has alternating double and single bonds around the six-member ring, but in which the double bonds are *isolated* from each other) is based on

(a) molecular mechanics calculations. (b) quantum mechanics calculations. (c) heats of hydrogenation of benzene and cyclohexene. (d) the difference in boiling point between benzene and cyclohexene.

13. Of the two hydrocarbons (I&II) shown, list the stronger acid (first) and of the two heterocycles (III&IV) list the stronger base (second).



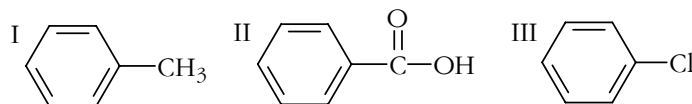
(a) I, III, (b) I, IV, (c) II, III, (d) II, IV, (e) Bogus question, dude! None of these compounds is acidic or basic.

14. Which of the following statements is *not* true of benzene?

(a) All the carbon-carbon bonds are of the same length.
 (b) Three and only three isomers of dimethylbenzene (xylene) are possible, not counting conformational isomers.
 (c) It has six π -electrons in bonding orbitals.
 (d) All the carbons are sp^2 hybridized.
 (e) Its carbons and hydrogens lie in a common plane.
 (f) Bogus question, dude. All of the above statements are true.

15. Rank the following three compounds in order of decreasing reactivity toward ring bromination (most reactive first).

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



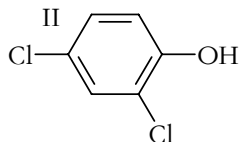
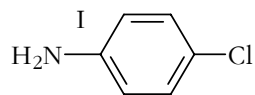
16. Again consider the three compounds in question #15. Select the answer that correctly indicates the major products that would be obtained by monobromination of the rings.

Answer	ortho + para isomers	meta isomer
(a)	I	II & III
(b)	I & II	III
(c)	I, II & III	(none)
(d)	(none)	I, II & III
(e)	I & III	II

17. Which of the following compounds would not be a good candidate for providing the ethyl group in a Friedel-Crafts type alkylation reaction that would convert benzene to ethylbenzene.

(a) ethane, (b) ethylene, (c) ethanol, (d) chloroethane.

18. Predict the major monoalkylation products you would expect to obtain from reaction of each of the following substances with chloromethane and anhydrous AlCl_3 .



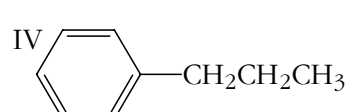
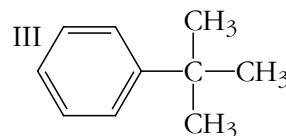
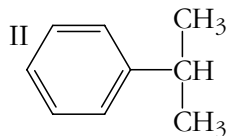
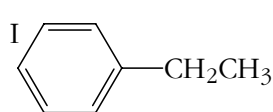
(a) I \rightarrow *p*-methylaniline; II \rightarrow 2,4-dichloro-5-methylphenol.

(b) I \rightarrow 4-chloro-3-methylaniline; II \rightarrow 2,4-dichloro-6-methylphenol.

(c) I \rightarrow 4-chloro-2-methylaniline; II \rightarrow 2,4-dichloro-5-methylphenol.

(d) I \rightarrow no reaction; II \rightarrow 2,4-dichloro-6-methylphenol.

19. Consider the four compounds shown below. Which of these compounds could not be synthesized in good yield by carrying out a Friedel-Crafts alkylation on benzene?

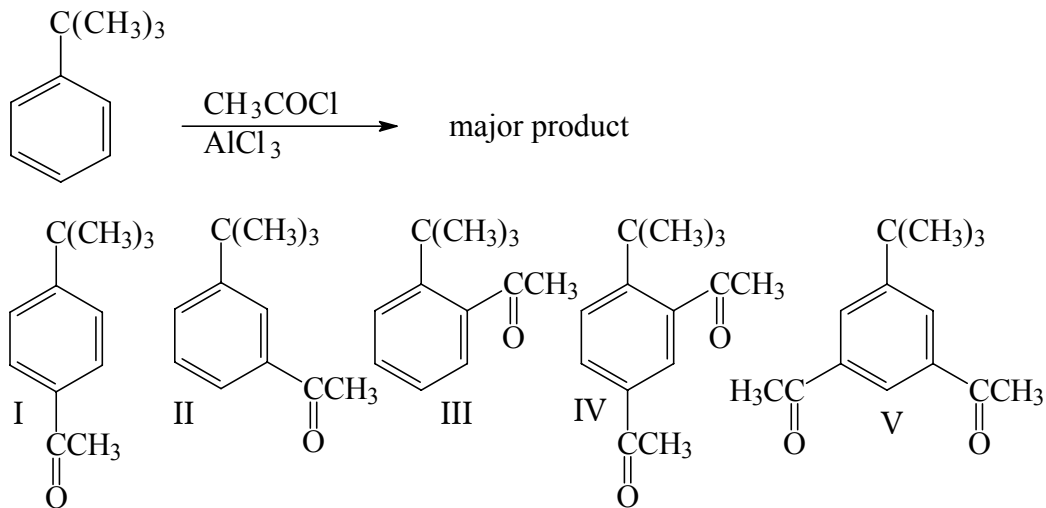


(a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV

20. Consider the four compounds shown in question #19. Which of these compounds could not be synthesized in good yield by carrying out a Friedel-Crafts acylation on benzene, followed by an appropriate reduction of the ketone obtained?

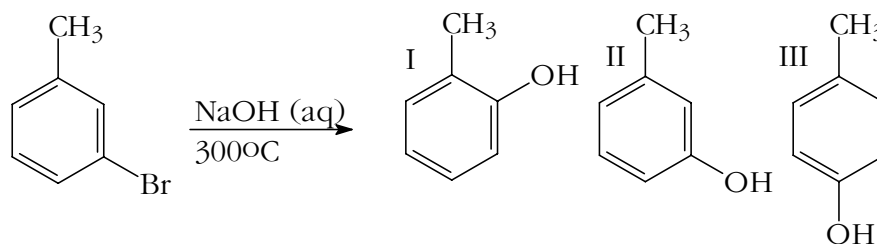
(a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV

21.



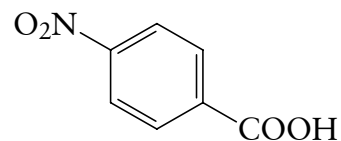
(a) I, (b) II, (c) III, (d) IV, (e) V, (f) Bogus question, dude. There would be no reaction.

22. Which products would actually form in the reaction shown to the right?



(a) I, (b) II,
 (c) III,
 (d) I & II,
 (e) I & III,
 (f) I, II & III, (g) There would be no reaction.

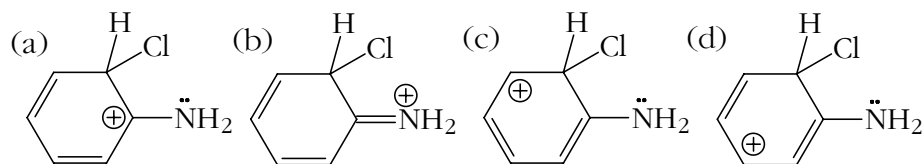
23. Which of the following synthetic procedures would be likely to be successful in making *p*-nitrobenzoic acid from benzene? [Note: (1) = first step, (2) = second step, *etc.*]



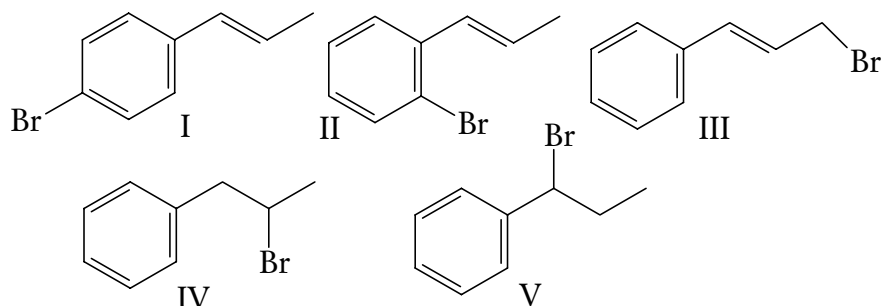
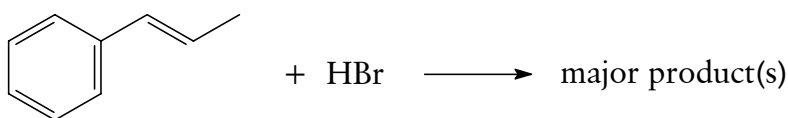
(I) (1) $\text{HNO}_3/\text{H}_2\text{SO}_4$, (2) HCOOH/KOH .
 (II) (1) $\text{HNO}_3/\text{H}_2\text{SO}_4$, (2) $\text{CH}_3\text{Br}/\text{AlCl}_3$, (3) $\text{KMnO}_4/\text{heat}$.
 (III) (1) HCOOH/KOH , (2) $\text{HNO}_3/\text{H}_2\text{SO}_4$.
 (IV) (1) $\text{CH}_3\text{Br}/\text{AlCl}_3$, (2) $\text{HNO}_3/\text{H}_2\text{SO}_4$, (3) $\text{KMnO}_4/\text{heat}$.
 (V) (1) $\text{CH}_3\text{Br}/\text{AlCl}_3$, (2) $\text{KMnO}_4/\text{heat}$, (3) $\text{HNO}_3/\text{H}_2\text{SO}_4$.

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

24. Which of the following resonance structures is *least* important to the stability of the intermediate that is formed when aniline undergoes electrophilic attack in ring chlorination at a position *ortho* to the NH₂ group?



25.



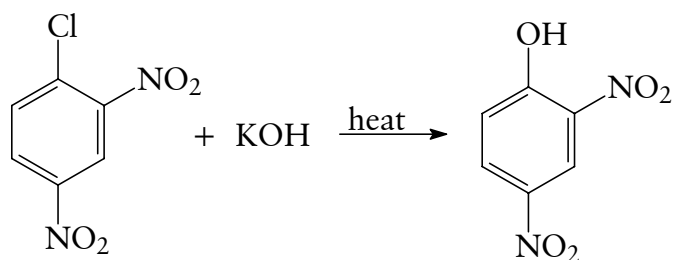
Answers

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

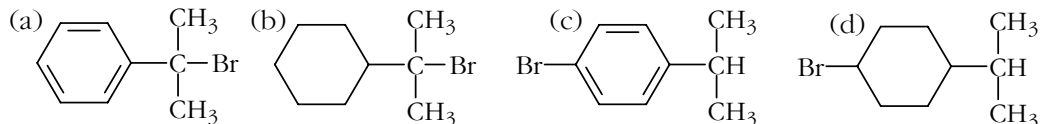
26.

The mechanism for this reaction involves

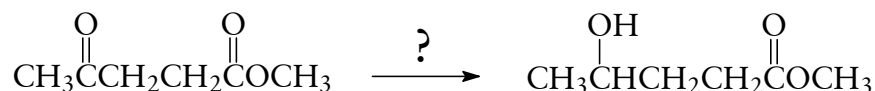
- (a) S_N1 substitution of Cl by OH.
 (b) S_N2 substitution of Cl by OH.
 (c) an elimination-addition sequence involving a substituted benzyne as an intermediate.
 (d) nucleophilic attack by OH⁻ at the chlorine-bearing carbon, resulting in the formation of a carbanion that subsequently loses Cl⁻.
 (e) electrophilic attack by OH⁻ at the chlorine-bearing carbon, resulting in the formation of a carbocation that subsequently loses Cl⁻.



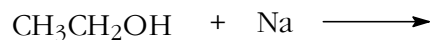
27. A mixture of equimolar amounts of isopropylbenzene, isopropylcyclohexane, and NBS (N-bromosuccinimide) is exposed to UV light. What is the major organic product isolated from the reaction mixture?



28. What reagent(s) would you use to accomplish the following reaction?



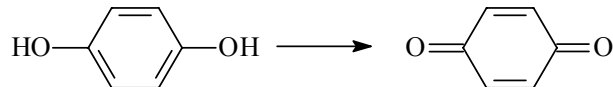
- (a) $\text{H}_3\text{O}^+/\text{H}_2\text{O}$, (b) (1) LiAlH_4 , (2) H_3O^+ , (c) (1) NaBH_4 , (2) H_3O^+ ,
 (d) (1) B_2H_6 , (2) $\text{H}_2\text{O}_2/\text{KOH}$, (e) H_2/Pd
29. Which of the following compounds can be reduced with lithium aluminum hydride to give 2-methyl-1-propanol, $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$?
- I: $(\text{CH}_3)_2\text{CHCH}_3$, II: $(\text{CH}_3)_2\text{CHCH}=\text{O}$, III: $(\text{CH}_3)_2\text{CHCOOH}$, IV: $(\text{CH}_3)_2\text{C}=\text{CH}_2$
 (a) I&II, (b) II&III, (c) III&IV, (d) II&IV, (e) I&III
30. Arrange the following compounds in order of decreasing acidity (most acidic first).
- I: $\text{CH}_2\text{CH}_2\text{OH}$, II: $\text{C}_6\text{H}_5\text{-OH}$, III: CH_3CH_3 , IV: CH_3COOH , V: $\text{C}_6\text{H}_5\text{-SO}_3\text{H}$
- (a) I>II>III>IV>V, (b) V>IV>III>II>I, (c) V>IV>I>II>III, (d) IV>V>II>I>III,
 (e) None of the above answers is correct.
31. Select the major product(s) of the following reaction.



- (a) $\text{CH}_3\text{CH}_2\text{O}^- \text{Na}^+ + \text{H}_2$ (b) $\text{CH}_3\overset{\text{O}}{\parallel}\text{CH} + \text{NaH}$ (c) $\text{Na}^+ \text{ } ^-\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2$
 (d) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + \text{NaOH} + \text{H}_2$ (e) No reaction takes place.

32. Which product would be formed, after workup with dilute sulfuric acid, when an excess of phenylmagnesium bromide, Ph-Mg-Br, reacts with methyl benzoate, PhCOOCH₃?
- (a) Ph₃C-OH, (b) Ph₂CH-OH, (c) Ph-CO-Ph, (d) Ph₃CH,
(e) Bogus query! Phenylmagnesium does not react with esters.
33. Which of the following procedures could be used to prepare a secondary (2°) 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.
34. 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: -COCH₃, III: -OH
- (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.
35. Which of the following reagents would be most successful at converting 1-butanol to butanal, CH₃CH₂CH₂CH=O?
- (a) KMnO₄, (b) CrO₃/H₂SO₄, (c) Na₂CrO₄/H₂SO₄, (d) C₅H₆NCrO₃Cl/CH₂Cl₂
36. The -OH group in phenol is more acidic than that in ethanol. This is mainly the result of
- (a) resonance stabilization that exists in phenol and not in ethanol.
(b) resonance stabilization that exists in ethanol and not in phenol.
(c) resonance stabilization that exists in the phenoxide anion and not in the ethoxide anion.
(d) resonance stabilization that exists in the ethoxide anion and not in the phenoxide anion.
37. An electron-withdrawing group attached to the ring of a phenol or to a carbon near the -OH group of an alcohol will
- (a) decrease the acidity of both. (b) increase the acidity of both.
(c) decrease the acidity of the alcohol but increase the acidity of the phenol.
(d) decrease the acidity of the phenol but increase the acidity of the alcohol.

38. The reaction to the right represents



- (a) the oxidation of hydroquinone to *p*-benzoquinone.
(b) the oxidation of *p*-benzoquinone to hydroquinone.
(c) the reduction of hydroquinone to *p*-benzoquinone.
(d) the reduction of *p*-benzoquinone to hydroquinone.

Do Not Detach The Following Sheets From The Rest Of The Exam

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.

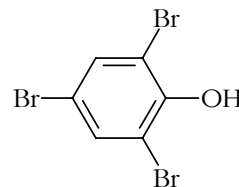
Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name is on the front sheet. Do not pass go. Do not collect two-hundred dollars.

1. **Synthesis.** Draw an outline for each of 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.

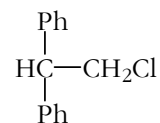
(a) Starting with benzene and using any other materials you require, outline a synthesis of *p*-nitrobromobenzene.



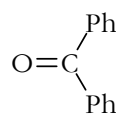
(b) Starting with benzene and using any other materials you require, outline a synthesis of 2,4,6-tribromophenol.



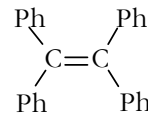
(c) Starting with 2-chloro-1,1-diphenylethane and benzophenone, outline a synthesis of 1,1,2,2-tetraphenylethene. You must employ a Grignard synthesis as part of your procedure.



2-chloro-1,1-diphenylethane



benzophenone

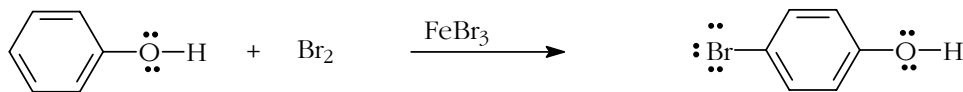


1,1,2,2-tetraphenylethene

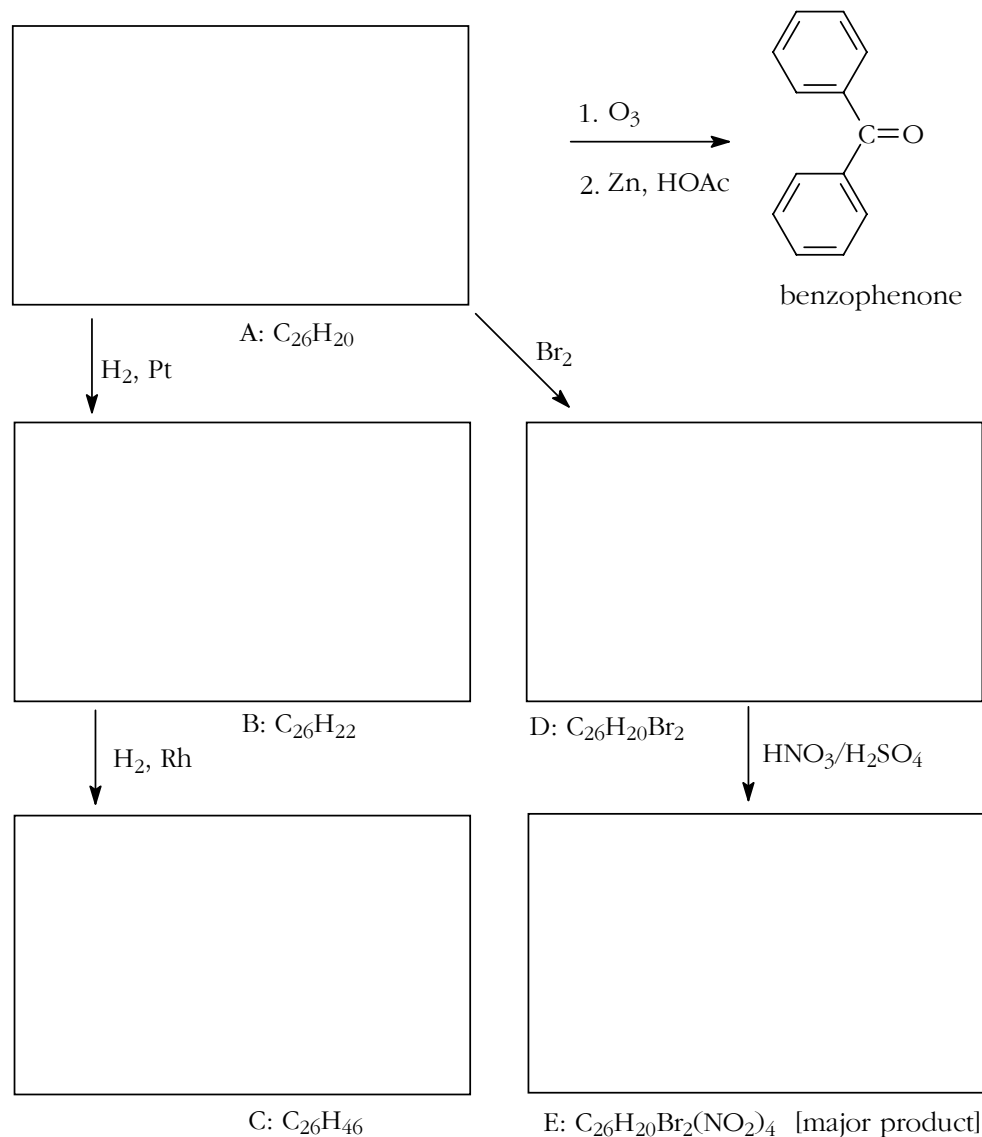
This question is in error. The halide starting material should have been chlorodiphenylmethane.

2. **Mechanism.**

Show the mechanism for the reaction shown below. Draw all important resonance structures of the intermediate σ -complex and indicate which makes the greatest contribution. Do not show transition states.



3. **Roadmap.** It's roadmap time! You are given some data about five compounds, A-E. Draw the structural formulas of A-E in the boxes provided. Compound A ($C_{26}H_{20}$) undergoes ozonolysis to give only benzophenone, and it reacts with hydrogen (platinum catalyst) to give compound B ($C_{26}H_{22}$). Compound B reacts with hydrogen (rhodium catalyst) to give compound C ($C_{26}H_{46}$). Compound A reacts with bromine to give D ($C_{26}H_{20}Br_2$). D reacts with a mixture of nitric and sulfuric acids to give mostly E ($C_{26}H_{20}Br_2(NO_2)_4$).



Please return the pencil.

Part 1 (76) _____

Part 2

1. (12) _____

2. (7) _____

3. (5) _____

Total (100) _____