Name______________________

Department of Chemistry
SUNY/Oneonta

Chem 322 - Organic Chemistry II
Examination #1 - February 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 Exam Booklet must be handed in and will be returned to you with a grade. Write your name in the space above NOW.

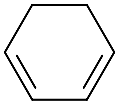
On the Test Scoring Answer Sheet, using a soft pencil, enter the following data (in the appropriate places):
\> your name, instructor's name,
\> your OSC student number, and
\> course number (30032201);
darken the appropriate bubbles under the entries, making dark black marks which fill the bubbles.

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.

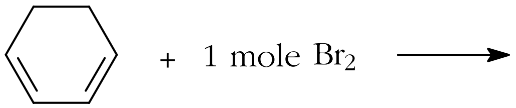
You have 50 minutes. Good luck!

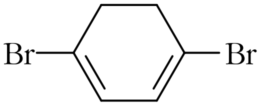
1. Select the correct IUPAC name for the compound shown to the right.



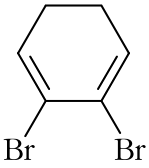
(a) benzene, (b) 1,3-cyclohexene, (c) 1,3-cyclohexadiene,
(d) 1,4-cyclohexene, (e) 1,4-cyclohexadiene

2. Select the principal organic product(s) of the following reaction.

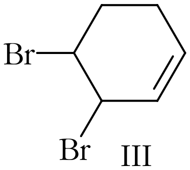




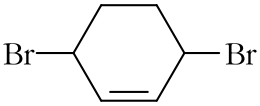
I



II



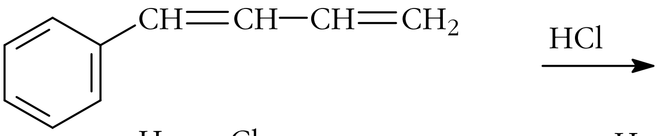
III



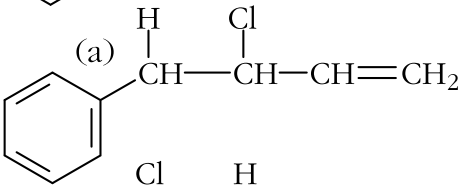
IV

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

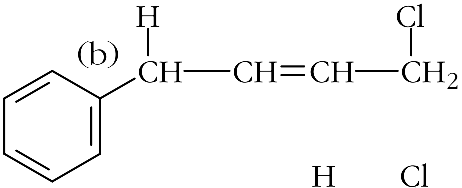
3. Select the product that would form in greatest amount when 1 mole of HCl reacts with 1-phenyl-1,3-butadiene.



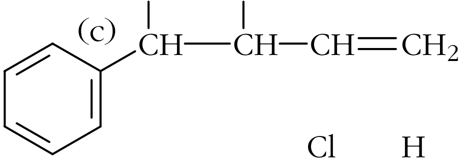
(a)



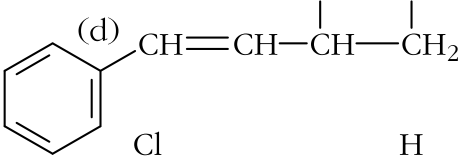
(b)



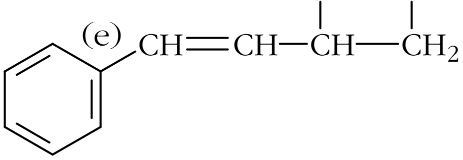
(c)



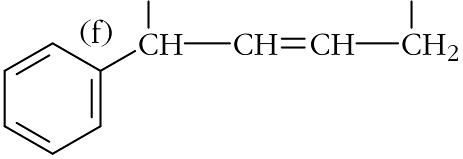
(d)



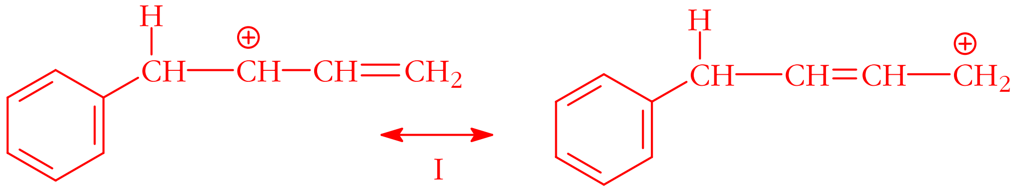
(e)



(f)

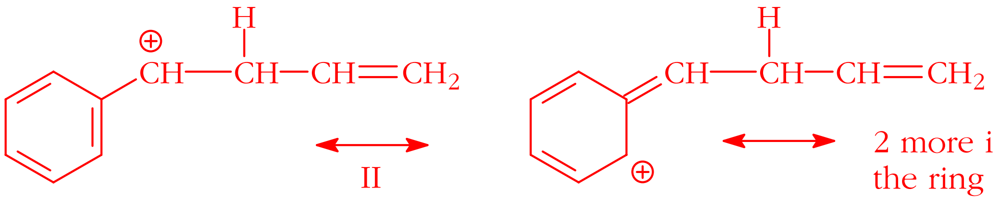


Compounds (a) and (b) derive from carbocation I which has two resonance structures, one primary, one secondary. This is an *allylic* carbocation.



I

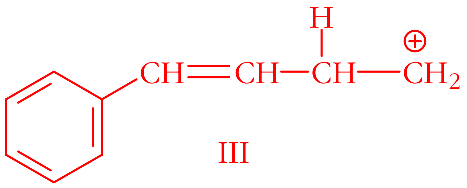
Compound (c) derives from carbocation II which has 4 resonance structures, one of which is seconday; the other three involve the benzene ring. This is a *benzylic* carbocation.



II

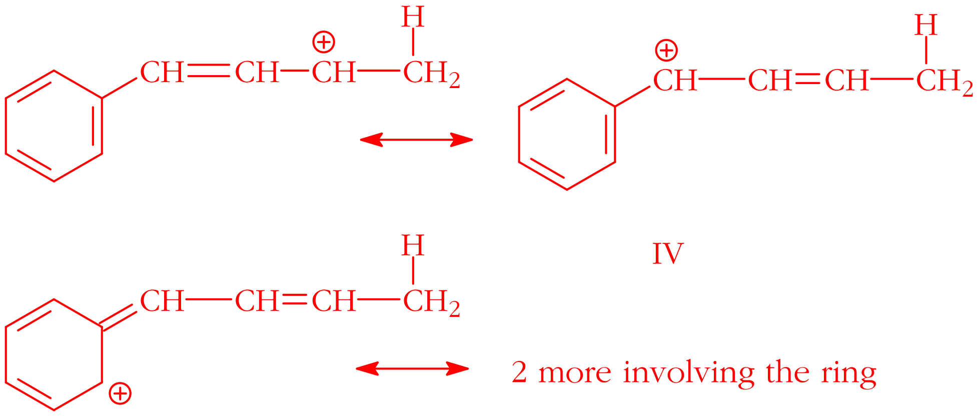
2 more involving the ring

Compound (d) derives from carbocation III which is a primary carbocation.



III

Compounds (e) and (f) derive from carbocation IV which has 5 resonance structures, two of which are secondary; the other three involve the benzene ring. This is an *allylic and benzylic* carbocation.

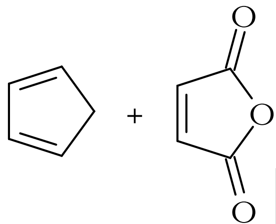


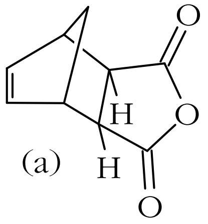
IV

2 more involving the ring

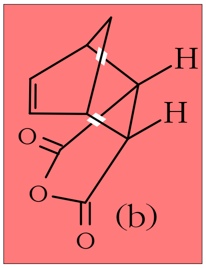
Since carbocation IV has the most resonance structures it should form the fastest which would make (e) or (f) the answer. Compound (e) is more stable than (f) however because it has a double bond that is conjugated with the π electrons of the ring. Therefore, (e) should be produced in greatest yield as carbocation IV picks up the chloride ion.

4. Which of the compounds shown would be the major product in the following reaction?

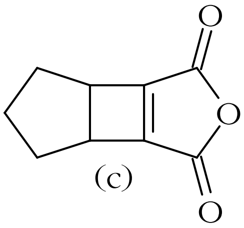


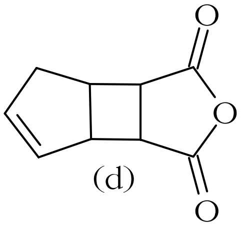


(a)



[✓ (b)]


(c)


(d)

The endo isomer predominates.

5. Which of the following statements is not true?

(a) Conjugated dienes are more stable than isolated dienes.
(b) Conjugated dienes undergo 1,4 as well as 1,2 additions.
[✓ (c) Conjugated dienes undergo 1,4 but not 1,2 additions.]
(d) Conjugated dienes are more reactive than isolated dienes.

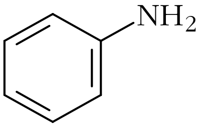
6. Aromatic compounds are obtained from bituminous coal by a process of

[✓ (a) distillation.] (b) extraction. (c) chromatography. (d) recrystallization.

7. Which of the following series of numbers represents the number of of π-electrons that could be found delocalized in conjugated monocyclic rings that are aromatic?

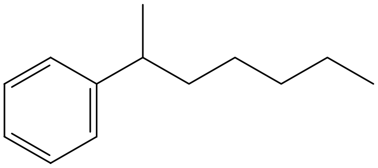
(a) 2, 4, 6, 8, ...; (b) 3, 5, 7, 9, ...; (c) 4, 8, 12, 16, ...; [✓ (d) 2, 6, 10, 14, ...]

8. The compound shown to the right is known as



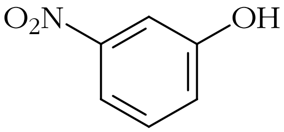
(a) toluene, (b) phenol, [✓ (c) aniline,] (d) benzaldehyde, (e) styrene

9. The IUPAC name for the compound shown to the right is



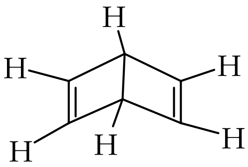
(a) 2-benzylheptane. (b) 2-phenylheptane.
(c) 2-heptylbenzene. (d) 1-methyl-1-phenylhexane.
(e) 1-methyl-1-benzylhexane.

10. An appropriate name for the compound shown to the right is



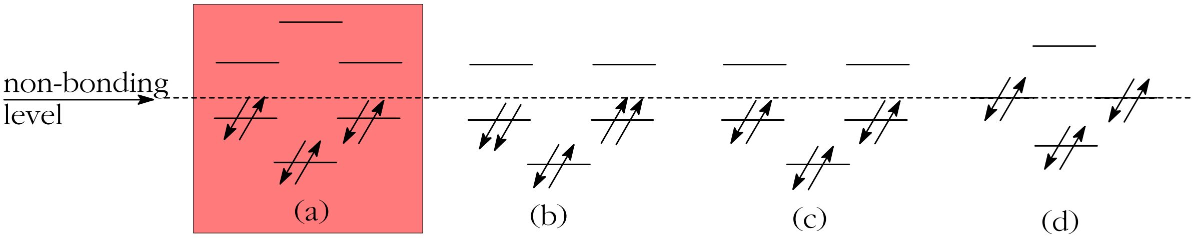
(a) *p*-nitrophenol. (b) *m*-nitrophenol.
(c) *o*-nitrophenol. (d) *p*-nitrophenyl.
(e) *m*-nitrophenyl. (f) *o*-nitrophenyl.

11. The compound shown to the right is known as Dewar benzene. What relationship does this compound bear to benzene?



(a) It is a resonance structure of benzene.
(b) It is an enantiomer of benzene.
(c) It is a diastereomer of benzene.
(d) It is a structural isomer of benzene.
(e) It bears no relationship to benzene.

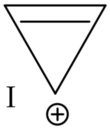
12. Which of the following is a representation of the π molecular orbitals in benzene ?



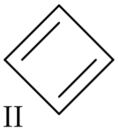
(e) none of the above

13. According to simple Huckel theory, which of the following rings should *not* be aromatic?

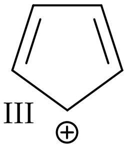
Note: Each carbon is bonded to one hydrogen in these structures.



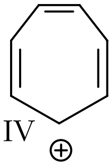
I



II



III



IV

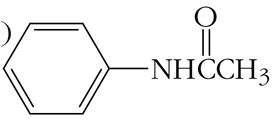
(a) I & II, (b) II & III, (c) III & IV,
(d) I & III, (e) II & IV,
(f) None of the above answers is correct.

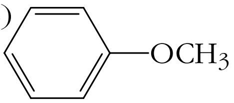
This is an application of the 4n+2 rule.

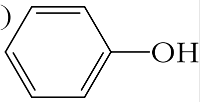
14. Benzene is most prone to undergo which of the following?

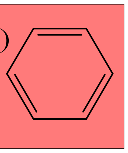
(a) electrophilic addition, (b) nucleophilic addition,
(c) electrophilic substitution, (d) nucleophilic substitution

15. Which of the following compounds reacts most slowly with HNO_3/H_2SO_4?

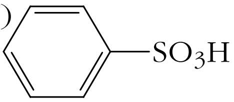
(a)


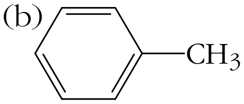
(b)


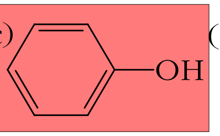
(c)


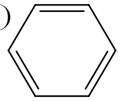
(d)


16. Which of the following compounds reacts most rapidly with HNO_3/H_2SO_4?

(a)


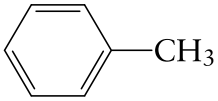
(b)


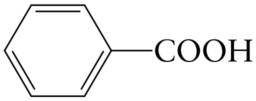
(c)


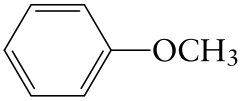
(d)


17. 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

I


II


III


18. Again consider the three compounds in question #17. 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

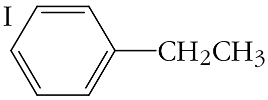
19. Which of the following compounds would not be a good candidates for providing the isopropyl group in an alkylation reaction that would convert benzene to isopropylbenzene.

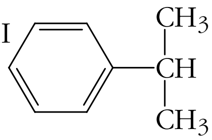
(I) propane, (II) 1-propene, (III) 2-propanol, (IV) 1-chloropropane

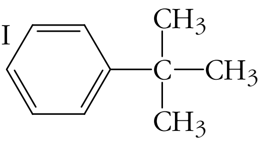
(a) I&II, (b) II&III, (c) III&IV, (d) I&IV

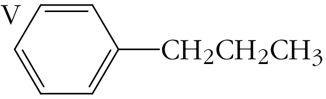
There is no simple way to convert propane to an isopropyl carbocation. 1-Chloropropane can be converted to the propyl carbocation. Some of these would rearrange to the isopropyl carbocation giving isopropylbenzene, but some would not, so a substantial amount of propylbenzene would form.

20. 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?

I


II


III


IV


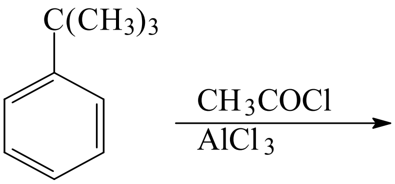
(a) I, (b) II, (c) III, (d) IV, (e) I&IV, (f) II&III, (g) II-IV

To prepare IV by a Friedel-Crafts alkylation one might use 1-bromopropane but some propyl carbocations would rearrange to give isopropylbenzene (II).

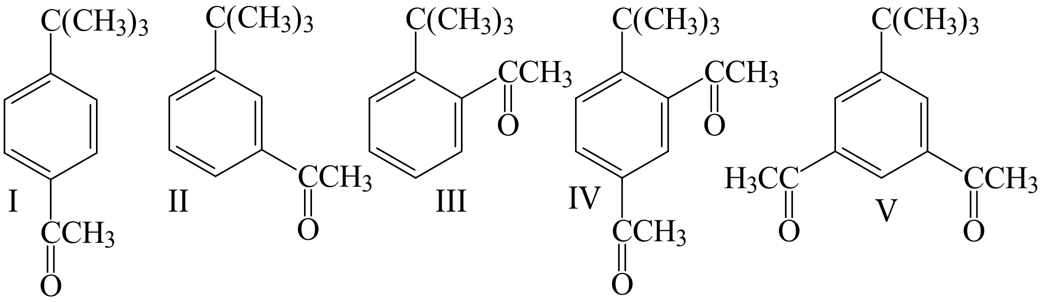
21. What is the electrophile in the desulfonation reaction of benzenesulfonic acid to give benzene?

(a) H^+ or H_3O^+, (b) benzene, (c) water, (d) Ph-SO_3^-, (e) SO_3

22.



major product

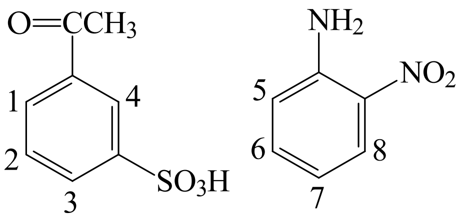


(a) I, (b) II, (c) III, (d) IV, (e) V, (f) no reaction

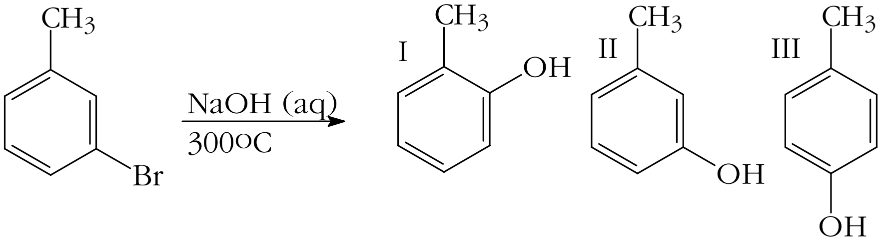
The *t*-butyl group is an ortho/para director electronically, but it is so large that steric interactions make it a para director in practice.

23. Which positions in these molecules would be good sites for electrophilic substitution?

(a) 1,3,4,5,6,7,8, (b) 2,5,7, (c) 1,3,5,7,
(d) 2,4,5,8, (e) 1,2,3,4,5,6,7

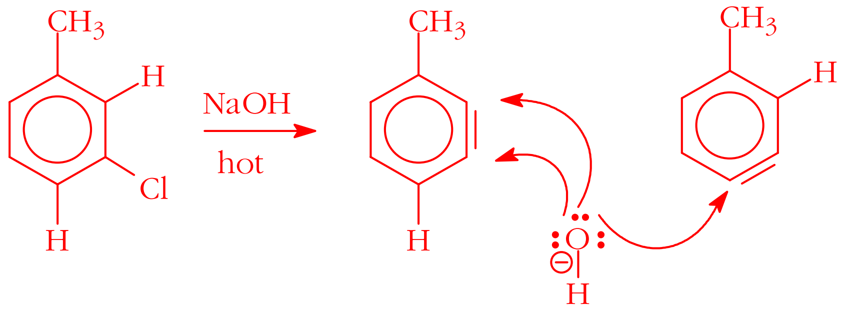


24. Which products would actually form in the reaction shown to the right?

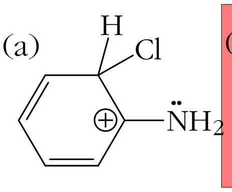


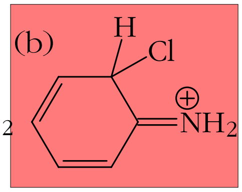
(a) I, (b) II,
(c) III,
(d) I & II,
(e) I & III,
(f) I, II & III, (g) There would be no reaction.

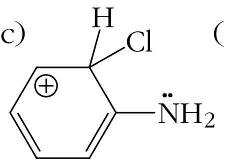
The benzyne π bond can form in two locations leading to three products:

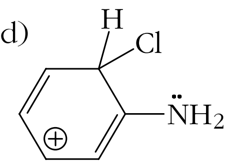


25. Which of the following resonance structures is *most* important to the stability of the intermediate that is formed when aniline undergoes electrophilic attack in ring chlorination at a position *ortho* to the NH_2 group?

(a)


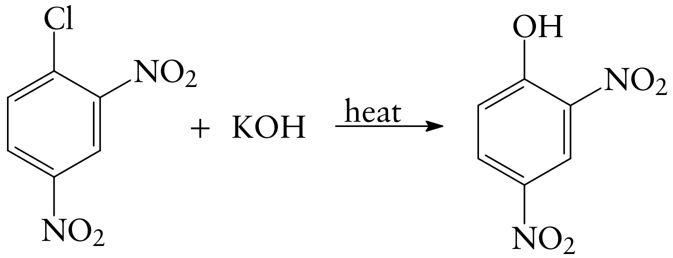
(b)


(c)


(d)


Every atom in (b) (except hydrogens) has an octet of electrons.

26. The mechanism for the reaction shown below 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 attach by OH^- at the chlorine-bearing carbon, resulting in the formation of a carbocation that subsequently loses Cl^-.

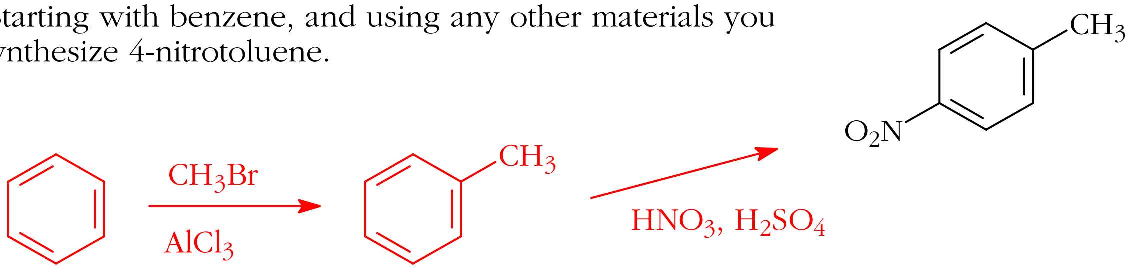
27. The purpose of the anhydrous aluminum chloride catalyst in the Friedel-Crafts alkylation is to

(a) form a reactive complex with the benzene ring.
(b) donate a pair of electrons to the alkyl halide.
(c) accept a pair of electrons from the halogen of the alkyl halide.
(d) assist in the removal of a proton from the intermediate in the reaction.

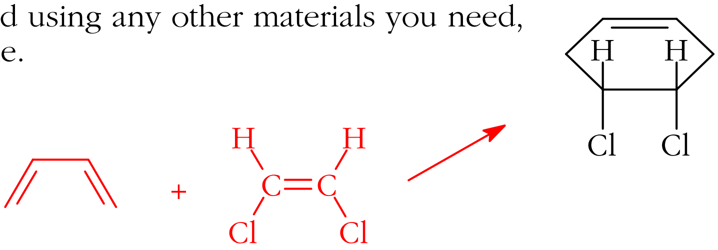
Part II. Enter your answers in the space provided. If there is inadequate room, continue on the back of the page and clearly indicate on the front of the page that you have done this. Hand in this entire exam booklet when you are finished; it will be returned to you with your grade. Make sure your name is on the front sheet.

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 need, synthesize 4-nitrotoluene.

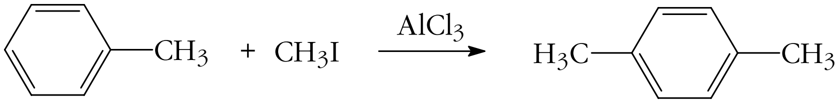


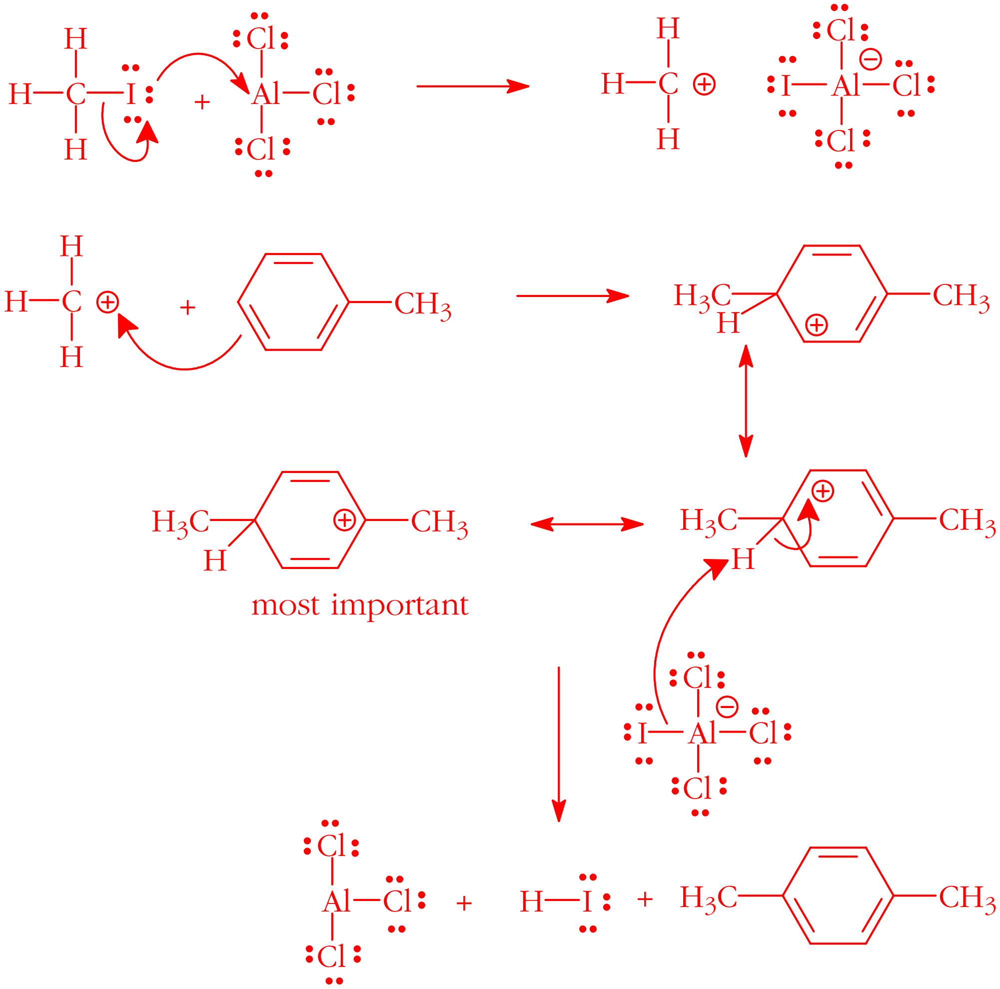
(b) Starting with 1,3-butadiene, and using any other materials you need, synthesize *cis*-4,5-dichlorocyclohexene.



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.




most important