

State University of New York at Stony Brook
Department of Chemistry

CHE 322, Organic Chemistry II

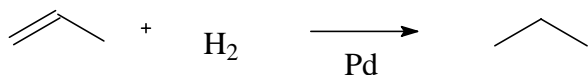
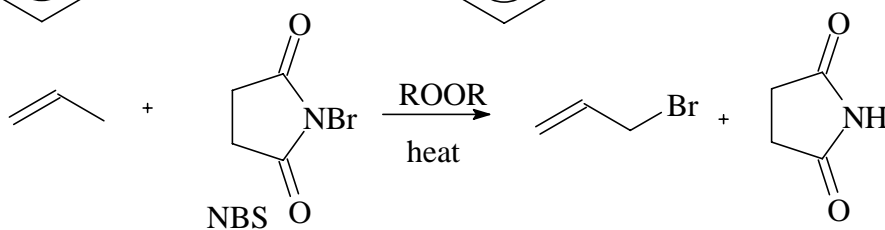
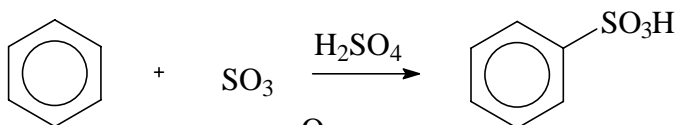
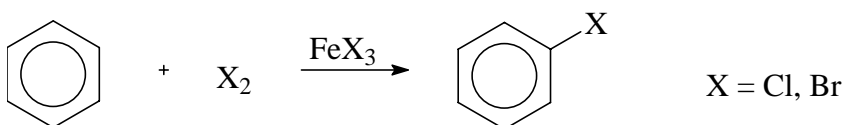
Exam I
Form 1

Feb. 17, 2004

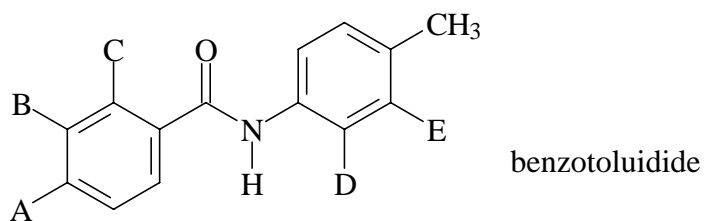
Please answer all questions specifically, concisely, and readably in the spaces provided on the answer sheet, which you will turn in. Think before writing. Include stereochemistry wherever relevant. Use the fronts and backs of the question pages for scratch work. Your Student Identification Number must be written and coded on the answer sheet, and your printed name and signature must be included at the upper right. Since the answer sheets will not be returned, we suggest that you record your answers on the question pages for comparison with the posted answers. Grades will be posted on Blackboard.

The first ten questions are multiple-choice. They are worth five points each. Enter your choices (only one per question) in spaces 1-10 of the answer sheet.

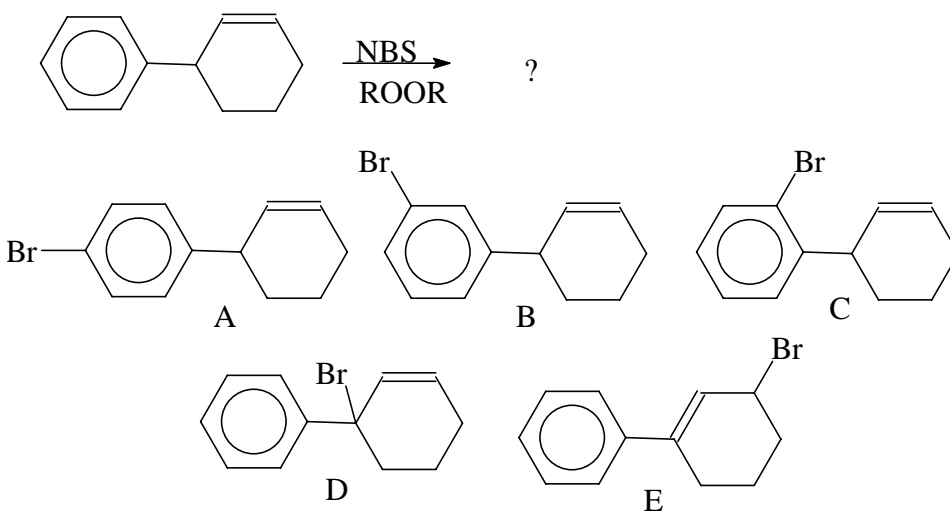
Some useful reactions:



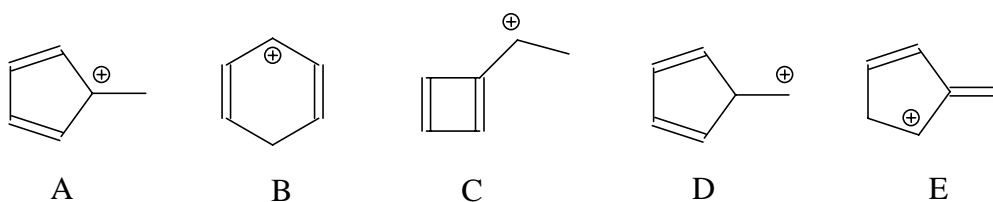
1. Which position of benzotoluidide, designated by the letters A-E, would most readily undergo chlorination on treatment with Cl_2 and FeCl_3 ?



2. Which of the products shown below would be the principal product produced in the reaction shown?

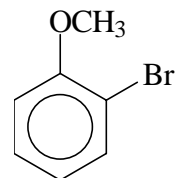


3. Which of the C_6H_7^+ carbocations shown below would be the most stable?



4. What would be the principal product of nitration of 2-bromoanisole?

- A. 2-nitroanisole
- B. 2-bromo-3-nitroanisole
- C. 2-bromo-4-nitroanisole
- D. 2-bromo-5-nitroanisole
- E. 2-bromo-6-nitroanisole

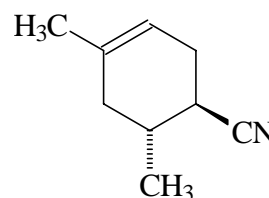


5. Which of the following sequences of reactions would be most effective for synthesizing *p*-nitrobenzoic acid from benzene? In each case, “methylation” means Friedel-Crafts reaction using methyl iodide and aluminum triiodide, “nitration” means treatment with a nitric acid-sulfuric acid mixture, and “oxidation” means heating with aqueous potassium permanganate solution.

- A. Nitration, then methylation, then oxidation
- B. Nitration, then oxidation, then methylation
- C. Methylation, then nitration, then oxidation
- D. Methylation, then oxidation, then nitration
- E. None of these reaction sequences would produce *p*-nitrobenzoic acid

6. What diene and dienophile would react to form the Diels-Alder product shown?

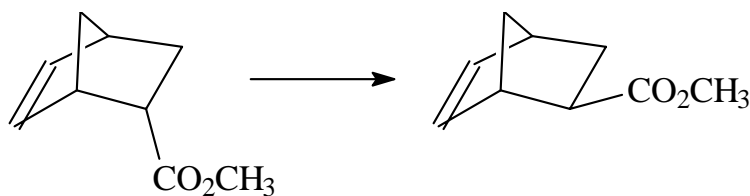
- A. 2-Methylbutadiene and *cis*-CH₃CH=CHCN
- B. 2-Methylbutadiene and *trans*-CH₃CH=CHCN
- C. 1,3-Pentadiene and *cis*-CH₃CH=CHCN
- D. 1,3-Pentadiene and *trans*-CH₃CH=CHCN
- E. 1,3-Cyclopentadiene and *trans*-CH₃CH=CHCN



7. A thermodynamically-controlled reaction will yield predominantly:

- A. the product whose formation requires the smallest free energy of activation.
- B. the product that can be formed in the fewest steps
- C. the product which possesses the greatest potential energy
- D. the most stable product
- E. the product that is formed at the fastest rate.

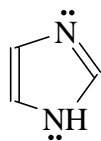
8. Upon prolonged heating, the endo Diels-Alder adduct shown below undergoes isomerization to form the exo adduct.



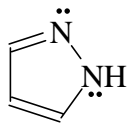
Which one of these statements about these compounds is **NOT** true?

- (A) The exo adduct is more stable than the endo adduct.
- (B) The endo adduct is formed under conditions of kinetic control.
- (C) The interconversion of exo and endo adducts shows the reversibility of the Diels-Alder reaction.
- (D) The exo and endo adducts are diastereomers.
- (E) The pure endo enantiomer shown yields the pure exo enantiomer shown when they interconvert.

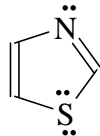
9. Which one of the heterocycles pictured below would **NOT** be aromatic?



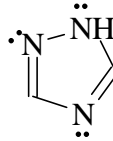
A



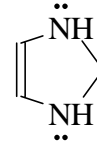
B



C



D



E

10. 1,3-Cyclopentadiene is an unusually acidic hydrocarbon because:

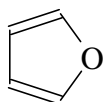
- (A) it readily gives Diels-Alder addition reactions;
- (B) formation of the conjugate base relieves ring strain;
- (C) cyclopentadiene is an aromatic compound;
- (D) the conjugate base is an aromatic carbanion;
- (E) the cyclopentadienyl cation is unusually stable.

Answers to questions 11 through 16 are to be entered into the designated places on the front and back of the answer sheet.

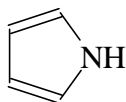
11. (8 points) Nitration occurs when benzene is treated with a mixture of nitric acid (HONO_2) and sulfuric acid (HOSO_2OH). Write the best Lewis structure for the electrophile, generated by reaction of nitric and sulfuric acids, which is responsible for the nitration reaction.

12. (10 points) Draw a structure for a conjugated diene that cannot function as a diene in a Diels-Alder reaction.

13. (10 points) Furan is a much more reactive Diels-Alder diene than pyrrole. Give a brief explanation for their relative reactivity.



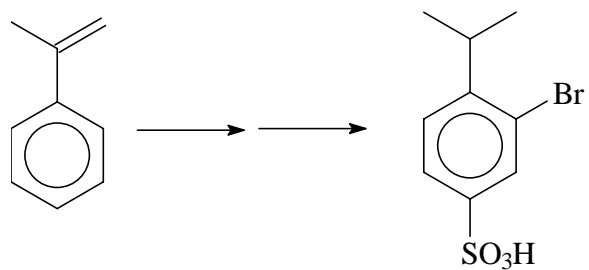
furan



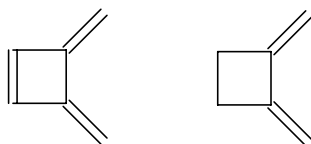
pyrrole

14. (10 points) Suggest a structure for the principal product formed by Friedel-Crafts alkylation of *p*-xylene, $p\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_3$, with neopentyl bromide, $(\text{CH}_3)_3\text{CCH}_2\text{Br}$.

15. (12 points) Suggest a practical synthetic route (more than one step) for carrying out the following conversion:



16. BONUS (10 points) Explain why triene A does not undergo Diels-Alder reaction with $\text{CH}_2=\text{CHCN}$, whereas diene B does.



A

B