

OpenCourseWare (2023)

CHEMISTRY II

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EXERCISES of Hydrocarbon Compounds: Alkanes, Alkenes, Alkynes, and Aromatic Hydrocarbons

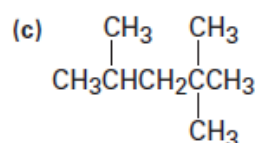
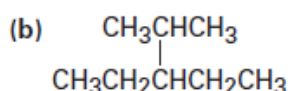
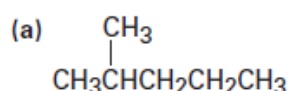


ALKANES AND THEIR STEREOCHEMISTRY

Exercise 1. How many isomers are there with the following descriptions?

- (a) Alcohols with the formula C_3H_8O
- (b) Bromoalkanes with the formula C_4H_9Br
- (c) Thioesters with the formula C_4H_8OS

Exercise 2. Identify the carbon atoms in the following molecules as primary, secondary, tertiary, or quaternary:



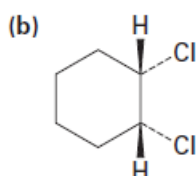
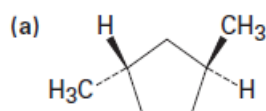
Exercise 3. Draw a qualitative potential-energy diagram for rotation about the C3-C4 bond in 2-methylpentane. Show Newman projections for all conformations located at the maximum and minimum points on your graph.

Exercise 4. Arrange the following conformations of 1,2-ethanediol in order of stability. Name the conformations using the prefixes *anti*, *syn*, and the suffixes *periplanar* and *clinal*.

Exercise 5. Draw the expected potential-energy diagram for the rotation about the C2-C3 bond in 2,3-dimethylbutane. Include the Newman projections of each staggered and eclipsed conformation.

CICLOALKANES

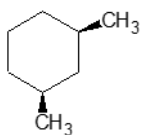
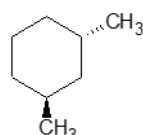
Exercise 6. Name the following substances, including the *cis*- or *trans*- prefix:



Exercise 7. How many $H \leftrightarrow H$ eclipsing interactions would be present if cyclopentane were planar? Assuming an energy cost of 4.0 kJ/mol for each eclipsing interaction, how much torsional strain would planar cyclopentane have? Since the measured total strain of cyclopentane is 26 kJ/mol, how much of the torsional strain is relieved by puckering?

Exercise 8. Draw two different chair conformations of trans-1,4-dimethylcyclohexane, and label all positions as axial or equatorial.

Exercise 9. Draw the chair conformations for the following disubstituted cycloalkanes. Justify which one is the most stable:

*cis*-1,2-dimethylcyclohexane*trans*-1,2-dimethylcyclohexane

Exercise 10. Draw the most stable chair conformation of cis-1-tert-butyl-4-chlorocyclohexane. Justify it by calculating the steric strain energy. Data. 1,3 diaxial strain: (H---Cl) = 1.0 kJ/mol; (H---C(CH₃)₃)-

Exercise 11. Draw both cis- and trans-1,4-dimethylcyclohexane in their more stable chair conformations.

(a) How many stereoisomers are there of cis-1,4-dimethylcyclohexane, and how many of trans-1,4-dimethylcyclohexane?

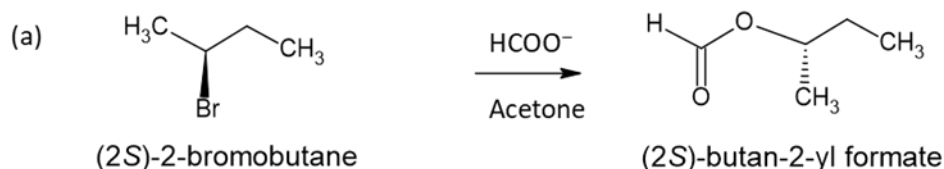
(b) Are any of the structures chiral?

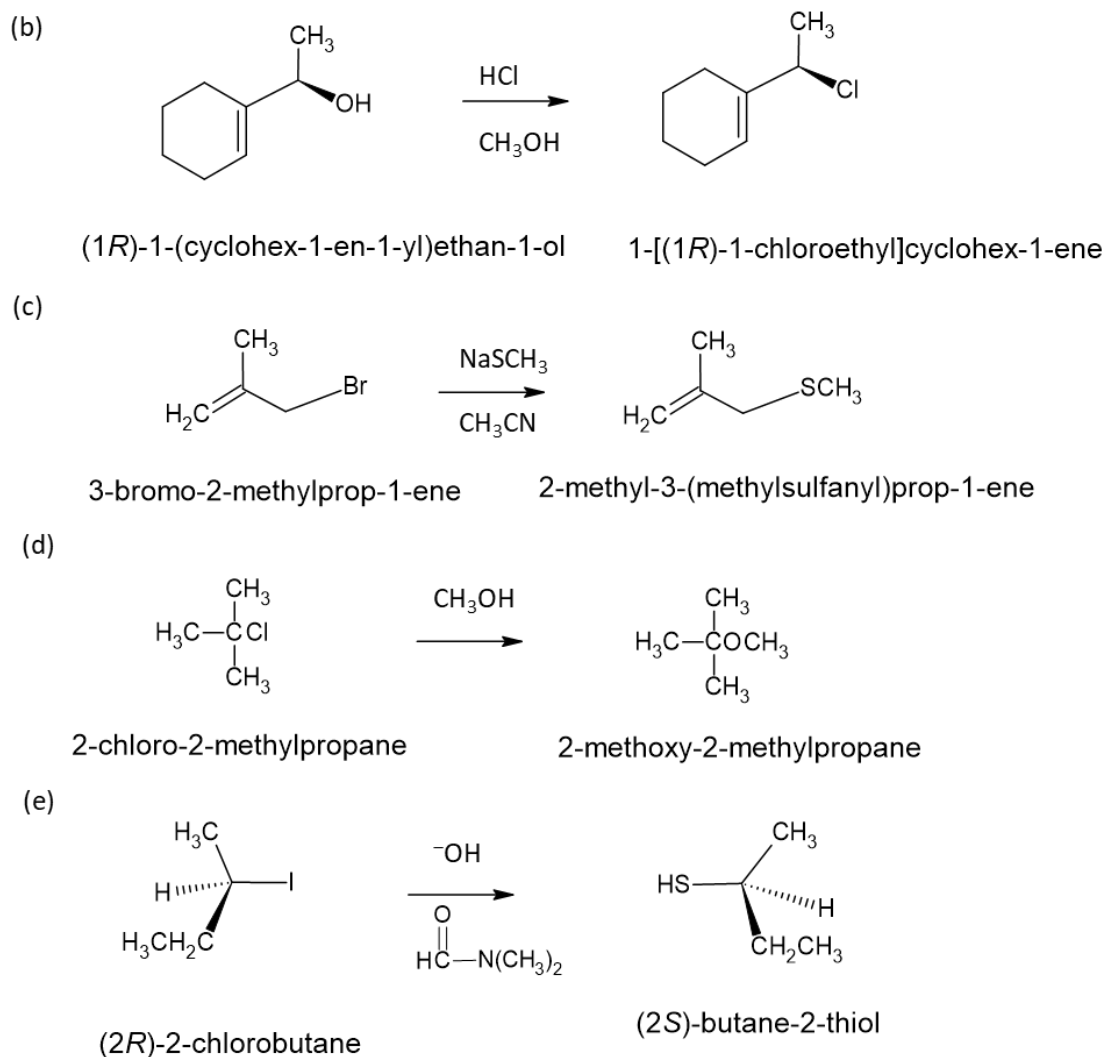
(c) What are the stereochemical relationships among the various stereoisomers of 1,4-dimethylcyclohexane?

REACTIONS OF ALKYL HALIDES

Exercise 12. What product would you expect from a nucleophilic substitution reaction of (*S*)-2-bromohexane with acetate ion (CH₃COO⁻)? Show the stereochemistry of both the reactant and product.

Exercise 13. Predict whether each of the following substitution reactions is likely to be S_N1 or S_N2:





Exercise 14. When 2-bromo-2-methylpropane is dissolved in aqueous ethanol at 25 °C, a mixture of $(\text{CH}_3)_3\text{COCH}_2\text{CH}_3$ (30%), $(\text{CH}_3)_3\text{COH}$ (60%), and $(\text{CH}_3)_2\text{C}=\text{CH}_2$ (10%) is obtained. Explain.

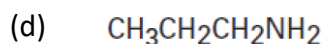
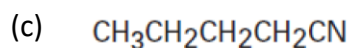
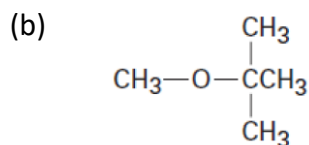
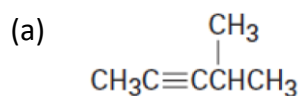
Exercise 15. Write the products of the following $\text{S}_{\text{N}}2$ reactions:

- (R) -3-chloroheptane + $\text{Na}^+ \text{SH}^-$
- (S) -2-bromooctane + $\text{N}(\text{CH}_3)_3$
- $(3R,4R)$ -4-iodo-3-methyloctane + $\text{K}^+ \text{SeCH}_3^-$

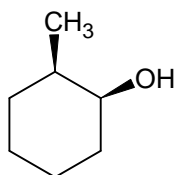
Exercise 16. Which compound in each of the following pairs will react faster in an $\text{S}_{\text{N}}2$ reaction with OH^- ?

- CH_3Br or CH_3I
- $\text{CH}_3\text{CH}_2\text{I}$ in ethanol or in dimethyl sulfoxide
- $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

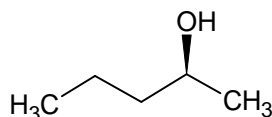
Exercise 17. How might you prepare each of the following molecules using a nucleophilic substitution reaction at some step?



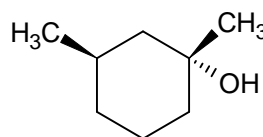
Exercise 18. Given that the dehydration of alcohols with H_2SO_4 (or H_3PO_4) in water proceeds through an E1 mechanism on secondary and tertiary substrates, indicate the major product for the dehydration of the following alcohols:



(1S,2R)-2-methylcyclohexan-1-ol

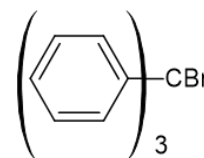
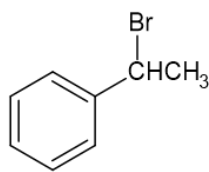
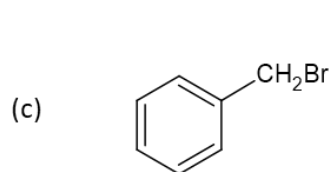
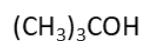
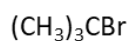
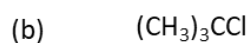
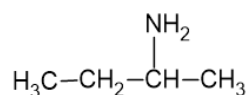
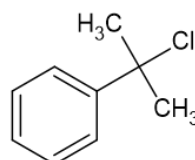
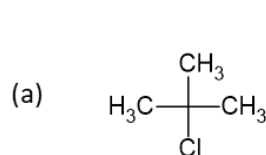


(2S)-pentan-2-ol

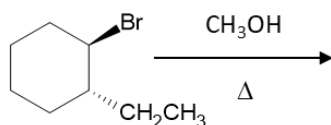


(1R,3R)-1,3-dimethylcyclohexan-1-ol

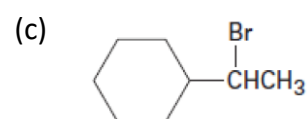
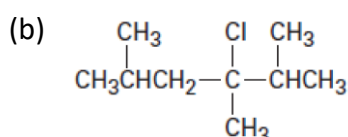
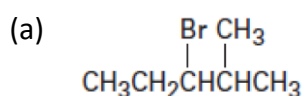
Exercise 19. Name and order each of the following sets of compounds with respect to $\text{S}_{\text{N}}1$ reactivity:



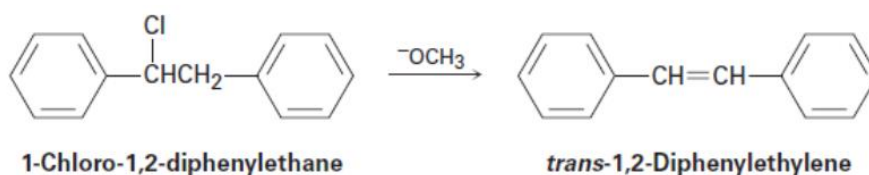
Exercise 20. Provide the major organic product of the substitution reaction below and a detailed stepwise mechanism which accounts for its formation:



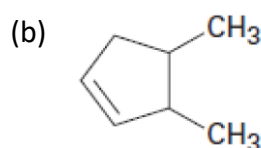
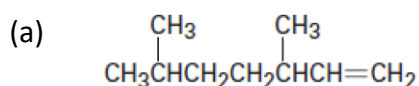
Exercise 21. Ignoring double-bond stereochemistry, what products would you expect from elimination reactions of the following alkyl halides? Which product will be the major product in each case?



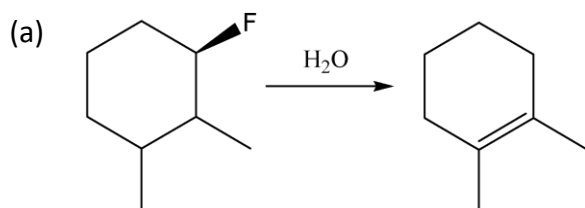
Exercise 22. 1-Chloro-1,2-diphenylethane undergoes E2 elimination to give either *cis*- or *trans*-1,2-diphenylethylene (stilbene). Draw Newman projections of the reactive conformations leading to both possible products and suggest a reason why the *trans* alkene is the major product.

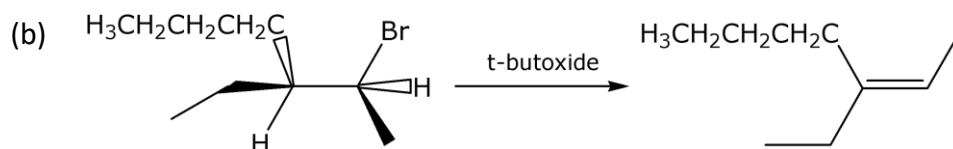


Exercise 23. What alkyl halides might the following alkenes have been made from?



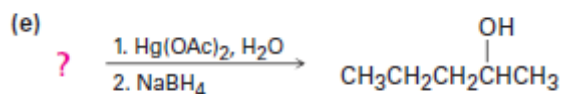
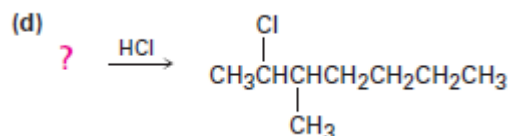
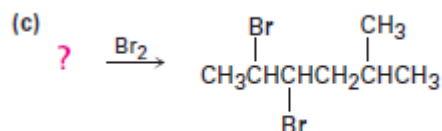
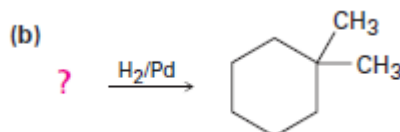
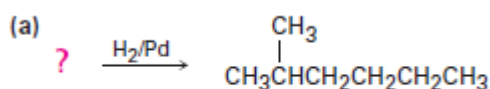
Exercise 24. Propose an elimination mechanism for the following reactions (E1 or E2). Pay special attention to stereochemistry.





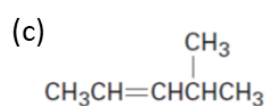
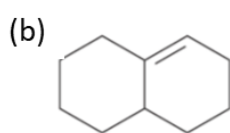
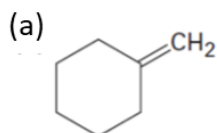
ALKENES AND ALKYNES

Exercise 25. Suggest structures for alkenes that give the following reaction products. There may be more than one answer for some cases.

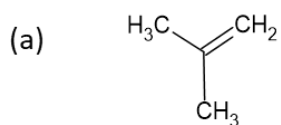


Exercise 26. E2 reaction of 2-bromo-2,3-dimethylbutane, $(\text{CH}_3)_2\text{CBrCH}(\text{CH}_3)_2$, yields two products, A and B, in a ratio of 79:21 using ethoxide in ethanol but in a ratio of 27:73 with *tert*-butoxide in 2-methyl-2-propanol. What are A and B? (b) Using $(\text{CH}_3\text{CH}_2)_3\text{CO}^-$ as a base results in an 8:92 ratio of A and B. Please explain this statement.

Exercise 27. Predict the major product of the addition of HBr to each of the following alkenes:



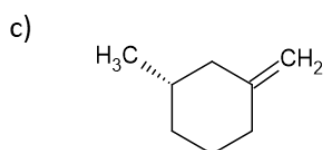
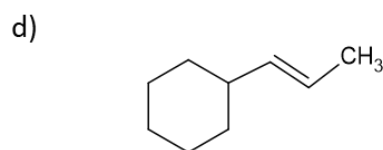
Exercise 28. Represent the major hydration product, of the following molecules. Give the IUPAC name.



2-methylprop-1-ene



1-methylcyclopent-1-ene

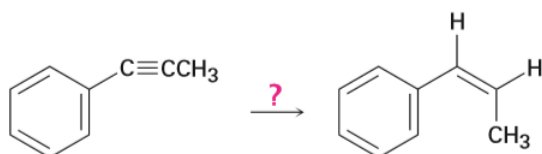
(1*S*)-1-methyl-3-methylidene cyclohexane[(1*E*)-prop-1-en-1-yl]cyclohexane

Exercise 29. How would you carry out the following reactions?

a)



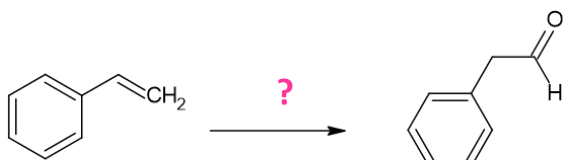
b)



c)



Exercise 30. How would you carry out the following conversion? More than one step is needed.

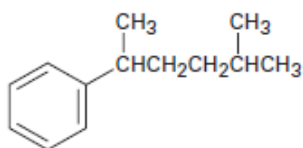
Ethenylbenzene
(styrene)

Phenylacetaldehyde

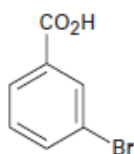
AROMATIC HYDROCARBONS

Exercise 31. Give IUPAC names for the following compounds:

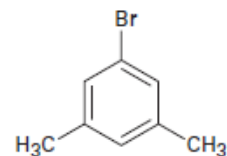
a)



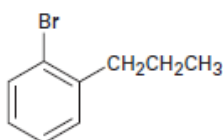
b)



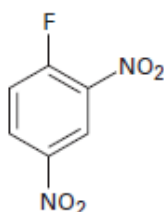
c)



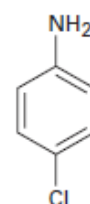
d)



e)



f)



Exercise 32. Predict the major product(s) of nitration of the following substances. Which react faster than benzene, and which slower?

- (a) Bromobenzene
- (b) Benzonitrile
- (c) Benzoic acid
- (d) Nitrobenzene

Exercise 33. How would you synthesize the following substances starting from benzene or phenol? Assume that ortho- and para-substitution products can be separated.

- (a) 2-bromobenzoic acid (*o*-bromobenzoic acid)
- (b) 1-methoxy-4-methylbenzene (*p*-Methoxytoluene)
- (c) 2,4,6-Trinitrobenzoic acid

Exercise 34. Complete the following sequence of reactions.

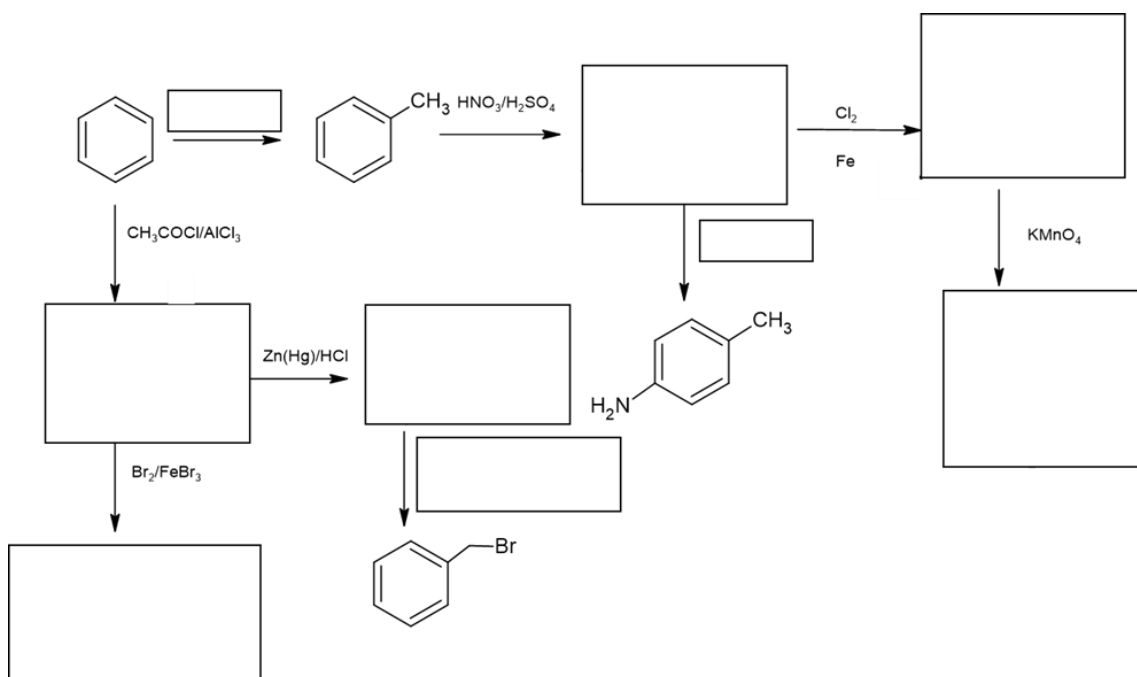


IMAGE CREDITS

- Images of all exercises were made by authors.