1. Problem 8.32b

Using the reagents below, list in order (by letter, no period) those necessary to transform 1-chlorobutane into 1-butyne. Note: Not all entry-fields provided may be needed. Choose "na" in any space where you have no reagent. **A.** H₂, Pt **B.** H₂, Lindlar's Catalyst **C.** H₂, Ni₂B(P-2) **D.** Br₂ **E.** NaNH₂, Mineral oil, heat **F.** NH₄Cl **G.** *t*-BuOK, *t*-BuOH, heat **H.** CH₃I **I.** CH₃CH₂I Step #1 Step #2 Step #3 Step #4

2. Problem 8.33

Starting with 2-methylpropene (isobutylene), select the correct reagent that will synthesize the following:

(a) OH

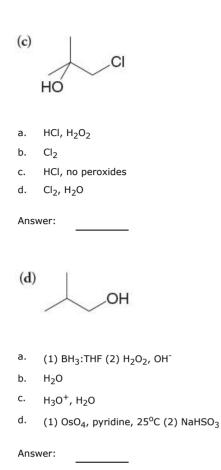
- a. (1) BH₃:THF (2) H₂O₂, OH⁻
- b. H₂O
- c. H₃O⁺, H₂O
- d. (1) OsO₄, pyridine, 25°C (2) NaHSO₃

Answer:

(b) Br

- a. HBr, H₂O₂
- b. Br₂
- c. HBr, no peroxides
- d. Br₂, H₂O

Answer:



3. Problem 8.31

Write structures for the major organic products from the following reactions. *Note: All structures should be drawn with no bonds between carbon and hydrogen.*



HBr (excess)

Cl₂ (1 equiv.)



(1) NaNH₂ (2) PhCH₂Br



Draw the product with the cycloalkane:

Draw the other organic product:

4. Problem 8.42

The reaction of bromine with cyclohexene involves anti addition, which generates, initially, the diaxial conformation of the addition product that then undergoes a ring flip to the diequatorial conformation of *trans*-1,2-dibromocyclohexane. However, when the unsaturated bicyclic compound **I** is the alkene, instead of cyclohexene, the addition product is exclusively in a stable diaxial conformation. Account for this. (You may find it helpful to build handheld molecular models.)

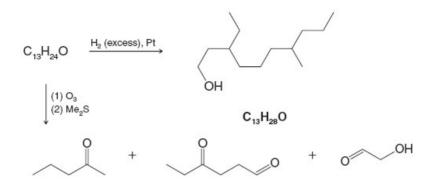


- a. Because of steric hindrance resulting from the methyl group present at the bridgehead, the diequatorial conformation is less stable than the diaxial conformation.
- b. The bulkiness of the bicyclic ring system requires more energy to produce a ring flip than that gained by assuming the diequatorial conformation.
- c. Eclipsing interactions introduce a barrier to rotation that is too great to be overcome, despite the more stable diequatorial conformation that would result from a ring flip.
- d. The fused nonhalogenated ring prevents the ring flip of the bromine-substituted ring necessary to give equatorial bromines.

Answer:

5. Problem 8.52

Pheromones are substances secreted by animals that produce a specific behavioral response in other members of the same species. Pheromones are effective at very low concentrations and include sex attractants, warning substances, and "aggregation" compounds. The sex attractant pheromone of the codling moth has the molecular formula $C_{13}H_{24}O$. Using information you can glean from the following reaction diagram, deduce the structure of the codling moth sex pheromone. The double bonds are known (on the basis of other evidence) to be (2*Z*,6*E*).



Structure of the codling moth sex pheromone:

6. Problem 8.54

Shown below is the final step in a synthesis of an important perfume constituent, *cis*-jasmone.



cis-Jasmone

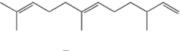
Which reagent(s) would carry out this last step? Select all that apply.

- a. H₂ and Ni
- b. H₂ and Pt
- c. Na, EtNH₂ followed by NH₄Cl
- d. H₂ and Lindlar's catalyst
- e. H₂ and Ni₂B(P-2)

Answer:

7. Problem 8.49

Farnesene (below) is a compound found in the waxy coating of apples.



Farnesene

(a)

What is the structure of the compound formed when farnesene is allowed to react with excess hydrogen in the presence of a platinum catalyst?

What is the IUPAC name for the product of part (a)?



How many stereoisomers of the product are possible?

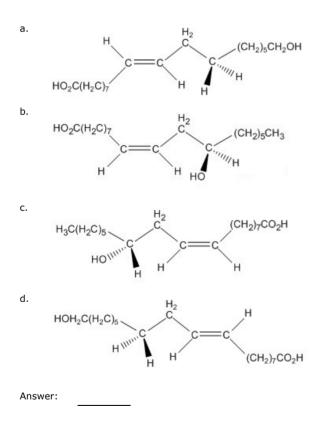
8. Problem 8.57

(b)

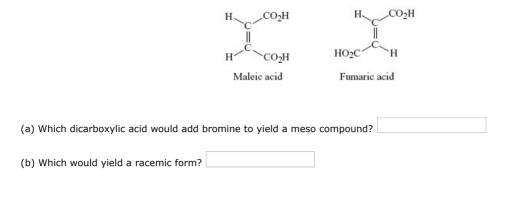
 $\label{eq:rescaled} \mbox{Ricinoleic acid, a compound that can be isolated from castor oil, has the structure CH_3(CH_2)_5CHOHCH_2CH = CH(CH_2)_7CO_2H.$

(a) How many stereoisomers of this structure are possible?

(b) Select the correct structure(s).

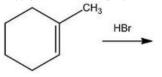


Using the structures below, predict the stereochemical outcome of the addition of bromine to maleic acid and to fumaric acid.



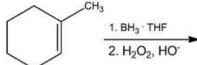
10. GO Tutorial: Determine product of alkene addition reaction with HBr

Supply the correct major product formed from the following reaction



11. GO Tutorial: Determine product from hydroboaration-oxidation reaction

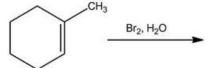
Supply the correct major product(s) formed from the following reaction



Note: Include stereochemistry in your answer. Draw both enantiomers.

12. GO Tutorial: Determine correct halohydrin product

Supply the correct major product formed from the following reaction



Note: Include stereochemistry in your answer. Draw both enantiomers.

13. Problem 8.39

Draw stereochemical formulas for the products that you would expect from each of the following reactions. If more than one stereoisomer is possible, draw any one of them. (You may find models helpful)

(1) OsO4 (a) (2) NaHSO, H2O (1) OsO4 (b) (2) NaHSO,, H,O Br₂ (c)

 Br_2

14. Problem 9.22

(d)

How many ^{1}H NMR signals (not peaks) would you predict for the following compound? (Consider all protons that would be chemical shift nonequivalent.)



signals

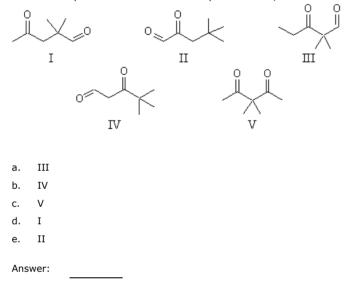
15. Testbank Question 20

For the following compound how many different signals would you see in the proton NMR? (Assume that you can see them all.)

C	\sum
a.	2
b.	3
c.	4
d.	5
e.	1
Answer:	

16. Testbank Question 47

The ^{1}H NMR spectrum of which of the compounds below, all of formula $C_{7}H_{12}O_{2}$, would consist of two singlets only?



17. Problem 9.25a

Propose structures for the compound G whose ${\rm ^{1}H}$ NMR spectra is shown in Figs. 9.47.

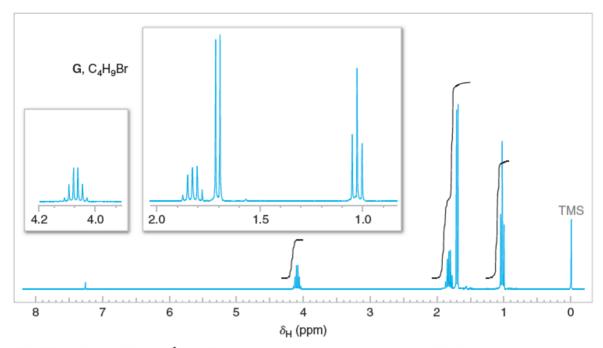


FIGURE 9.47 The 300-MHz ¹H NMR spectrum of compound **G**, Problem 9.25. Expansions of the signals are shown in the offset plots.

Draw the structure of G. Note: All structures should be drawn with no bonds between carbon and hydrogen.

18. Testbank Question 62

What is the structure of the compound in the following 1 H-NMR spectrum with the molecular formula C₁₀H₁₂O₂? Relative integration is shown.

