Study Guide and Solutions Manual

Organic Chemistry
A Brief Course

THIRTEENTH EDITION

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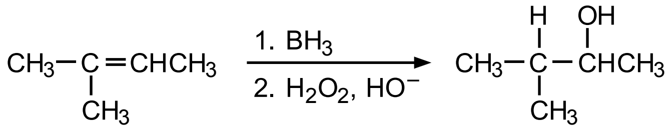
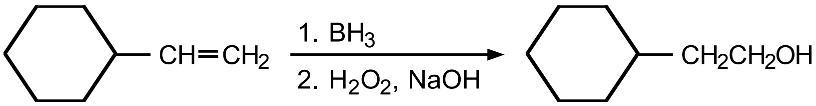
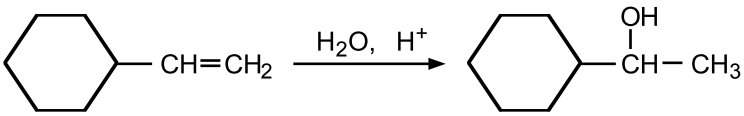


3.20

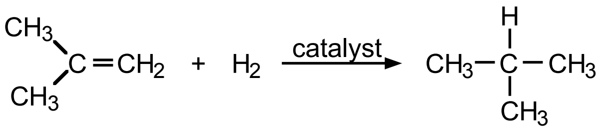


Acid-catalyzed hydration of vinylcyclohexane occurs in the Markovnikov sense:

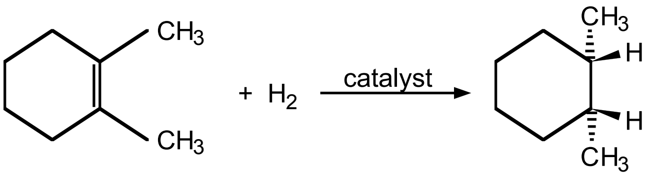


vinylcyclohexane

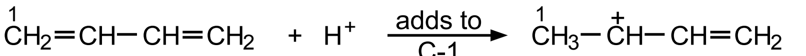
3.21 a.



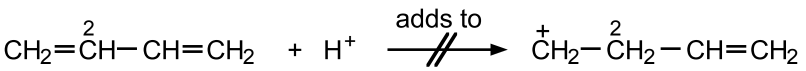
b.



3.22

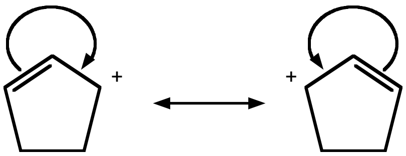


allylic carbocation, stabilized by resonance

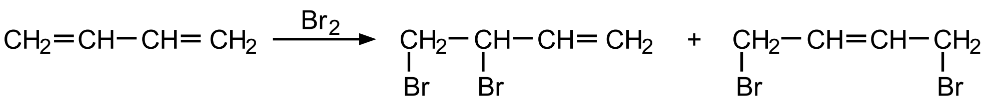


primary carbocation, much less stable than the allylic carbocation

3.23



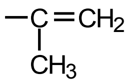
3.24



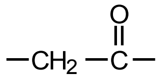
1,2-addition   1,4-addition

3.25 To find the structures of the diene and dienophile, break the cyclohexene ring just beyond the ring carbons that are connected to the double bond (the allylic carbons):

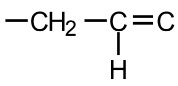
and the configuration is *S*. A word about the priority order may be helpful. The



group has three bonds from the attached carbon atom to the next atoms "out" and is therefore of the highest priority. The remaining groups both begin with –CH_2, so we must proceed further. One group is

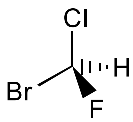


and the other is

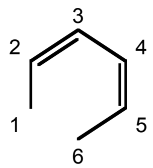


Of these, the group with C=O has the higher priority because oxygen has a higher atomic number than carbon.

5.38 The priority of the four groups is Br > Cl > F > H. The structure of the *R* enantiomer is:

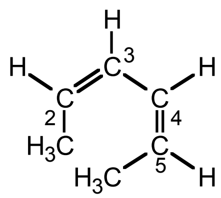


5.39 a.



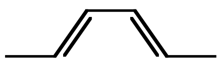
(*Z*,*Z*)-2,4-hexadiene or more precisely, (2Z,4*Z*)-2,4-hexadiene

If you have difficulty, draw the full structure:



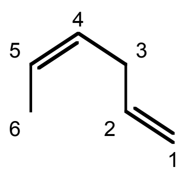
At the double bond between C-2 and C-3, the priority order is CH_3 > H and CH_3CH=CH– > H. The two high-priority groups, CH_3 and CH_3CH=CH–, are *Z* or *zusammen*. The same is true at the double bond between C-4 and C-5.

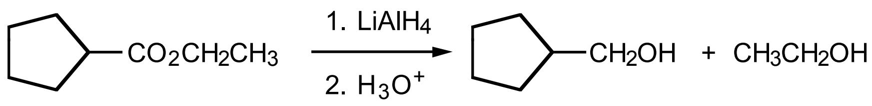
b.



(*E*,*E*)-2,4-hexadiene

c.

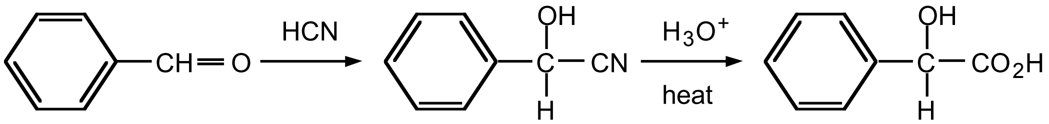




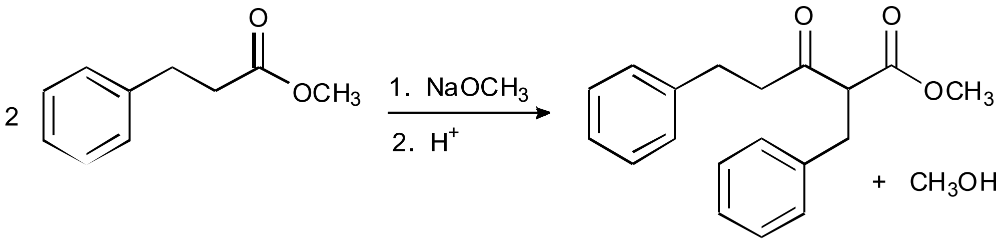
10.55 Ketones are more reactive toward nucleophiles than esters. Reduction therefore occurs at the ketone carbonyl group, to give

$$CH_3CH(OH)CH_2CH_2CO_2CH_3$$

10.56 The method combines the formation of a cyanohydrin (Sec. 9.10) with the hydrolysis of a cyanide to an acid (Sec. 10.7d).

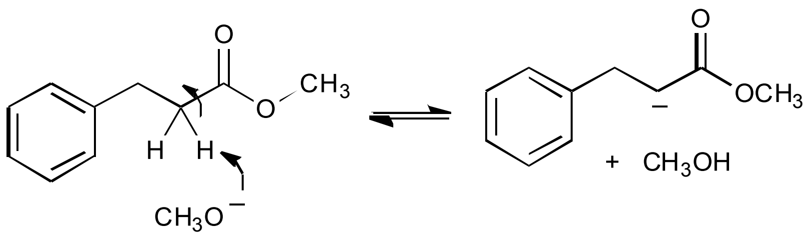


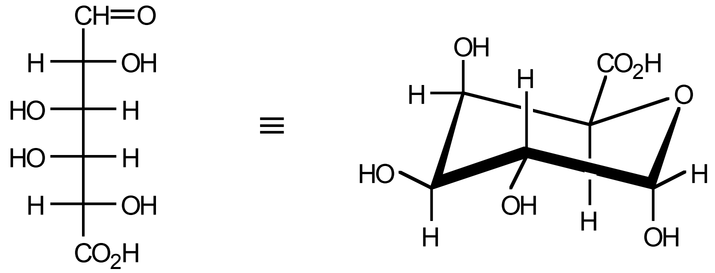
10.57 Use eqs. 10.48–10.50 as a guide. The overall equation is



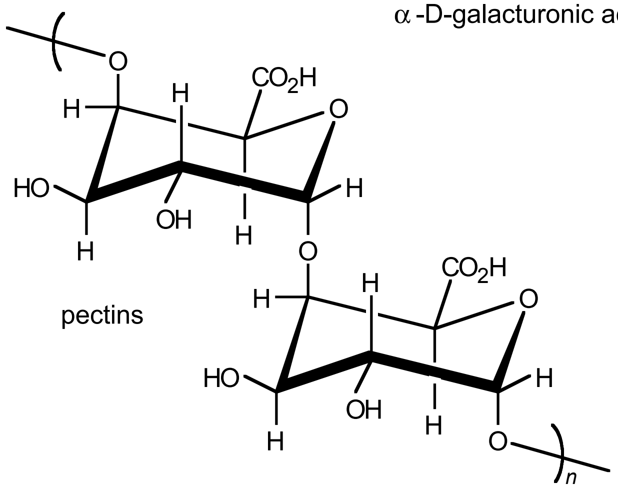
The steps are as follows:

<u>Step 1:</u>



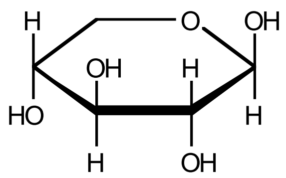


α-D-galacturonic acid

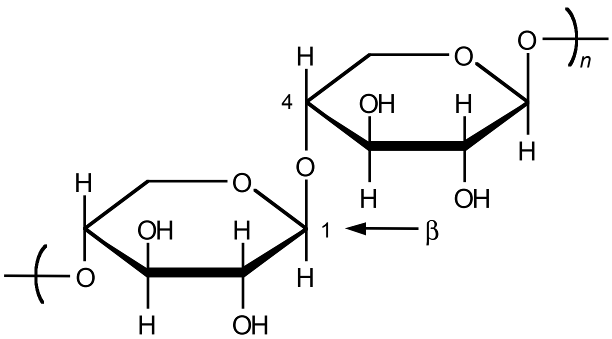


pectins

16.45 The formula for β-D-xylopyranose, derived from the Fischer projection of D-xylose in Figure 16.1, is



Since the xylans have these units linked 1,4, their structure is



16.46 The anomeric carbon of the glucose unit on the "right" is in equilibrium with the corresponding aldehyde. This will be oxidized by the Br_2 to the corresponding acid. Subsequent treatment with aqueous acid will then hydrolyze the glycosidic bond.