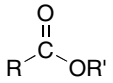
Chapter 29: Lipids

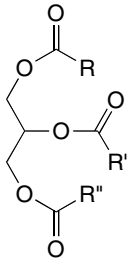
♦ Hydrolyzable lipids

[1] Waxes (29.2)—Esters formed from a long-chain alcohol and a long-chain carboxylic acid



R, R' = long chains of C's

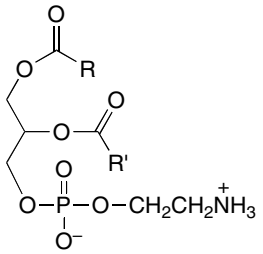
[2] Triacylglycerols (29.3)—Triesters of glycerol with three fatty acids



R, R', R" = alkyl groups with 11–19 C's

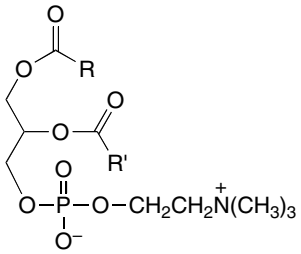
[3] Phospholipids (29.4)

[a] Phosphatidylethanolamine (cephalin)



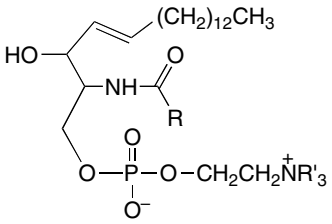
R, R' = long carbon chain

[b] Phosphatidylcholine (lecithin)



R, R' = long carbon chain

[c] Sphingomyelin



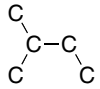
R = long carbon chain
R' = H or CH_3

♦ Nonhydrolyzable lipids

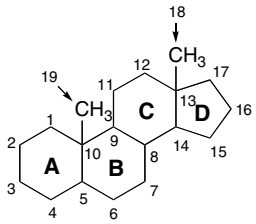
[1] Fat-soluble vitamins (29.5)—Vitamins A, D, E, and K

[2] Eicosanoids (29.6)—Compounds containing 20 carbons derived from arachidonic acid. There are four types: prostaglandins, thromboxanes, prostacyclins, and leukotrienes.

[3] Terpenes (29.7)—Lipids composed of repeating five-carbon units called isoprene units

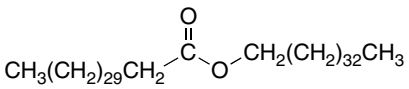
Isoprene unit	**Types of terpenes**			
	[1] monoterpene	10 C's	[4] sesterterpene	25 C's
	[2] sesquiterpene	15 C's	[5] triterpene	30 C's
	[3] diterpene	20 C's	[6] tetraterpene	40 C's

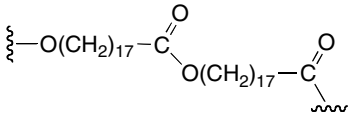
[4] Steroids (29.8)—Tetracyclic lipids composed of three six-membered and one five-membered ring



Chapter 29: Answers to Problems

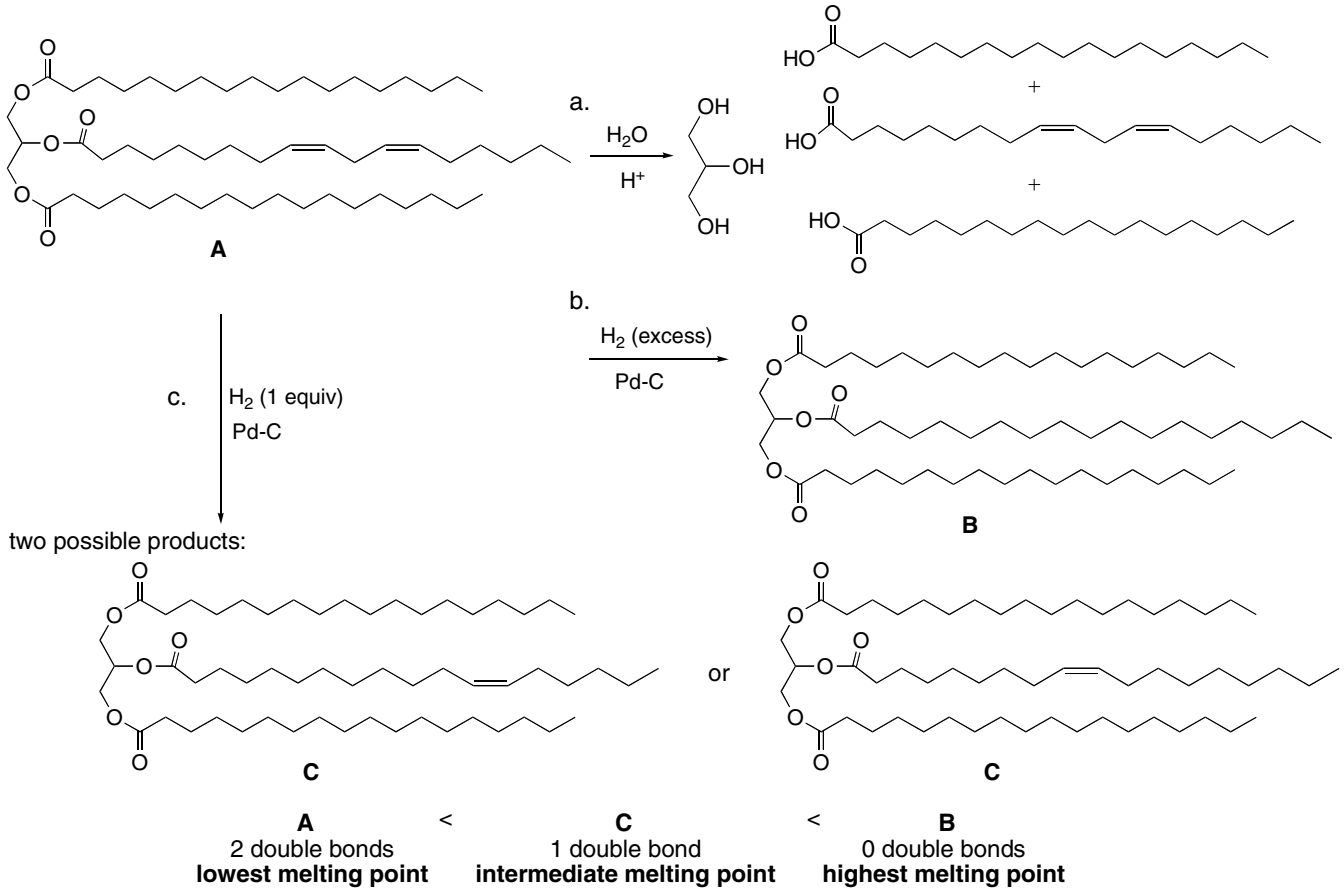
29.1 Waxes are esters (RCOOR') formed from a high molecular weight alcohol (R'OH) and a fatty acid (RCOOH).

a. 

b. 

29.2 Eicosapentaenoic acid has 20 C's and 5 C=C's. Since an increasing number of double bonds decreases the melting point, eicosapentaenoic acid should have a melting point lower than arachidonic acid; that is, < 49° C.

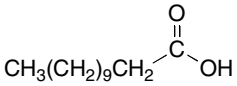
29.3



A < **C** < **B**

A	C	B
2 double bonds	1 double bond	0 double bonds
lowest melting point	**intermediate melting point**	**highest melting point**

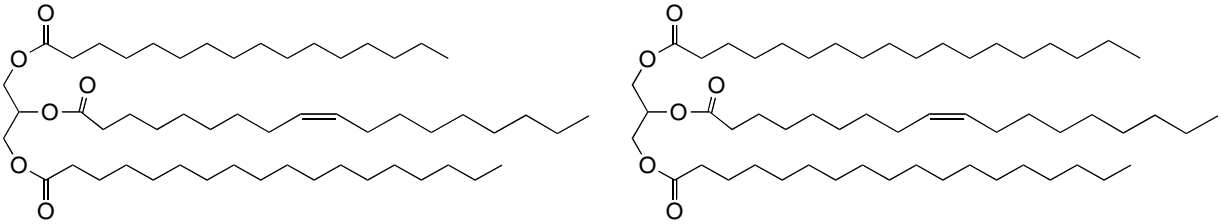
29.4



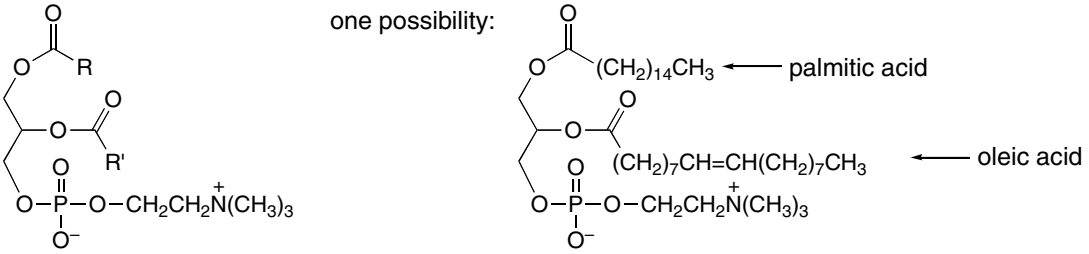
lauric acid

Lauric acid is a saturated fatty acid but has only 12 C's. The carbon chain is much shorter than palmitic acid (16 C's) and stearic acid (18 C's), making coconut oil a liquid at room temperature.

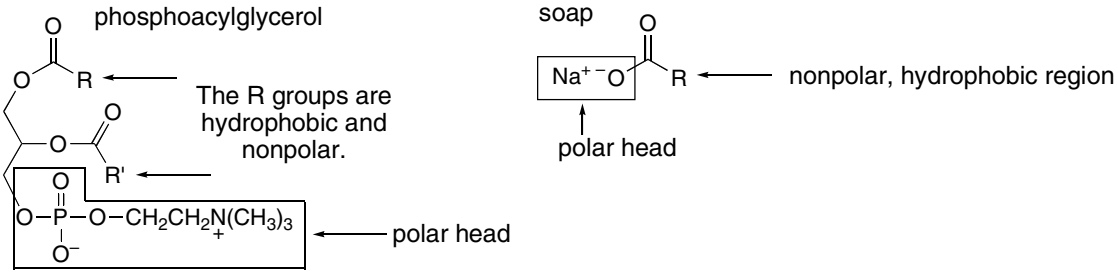
29.5



29.6 A lecithin is a type of phosphoacylglycerol. Two of the hydroxy groups of glycerol are esterified with fatty acids. The third OH group is part of a phosphodiester, which is also bonded to another low molecular weight alcohol.



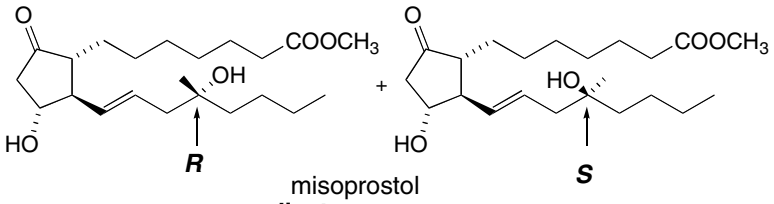
29.7 Soaps and phosphoacylglycerols have hydrophilic and hydrophobic components. Both compounds have an ionic "head" that is attracted to polar solvents like H_2O. This head is small in size compared to the hydrophobic region, which consists of one or two long hydrocarbon chains. These nonpolar chains consist of only C–C and C–H bonds and exhibit only van der Waals forces.



29.8 Phospholipids have a polar (ionic) head and two nonpolar tails. These two regions, which exhibit very different forces of attraction, allow the phospholipids to form a bilayer with a central hydrophobic region that serves as a barrier to agents crossing a cell membrane, while still possessing an ionic head to interact with the aqueous environment inside and outside the cell. Two different regions are needed in the molecule. Triacylglycerols have three polar, uncharged ester groups, but they are not nearly as polar as phospholipids. They do not have an ionic head with nonpolar tails and so they do not form bilayers. They are largely nonpolar C–C and C–H bonds so they are not attracted to an aqueous medium, making them H_2O insoluble.

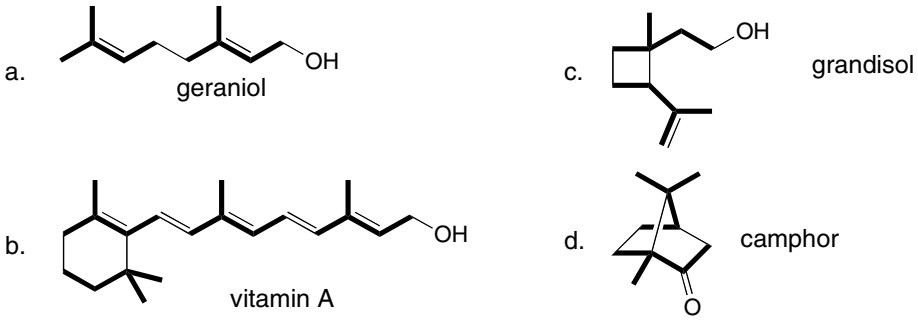
29.9 Fat-soluble vitamins are hydrophobic and therefore are readily stored in the fatty tissues of the body. Water-soluble vitamins, on the other hand, are readily excreted in the urine and large concentrations cannot build up in the body.

29.10

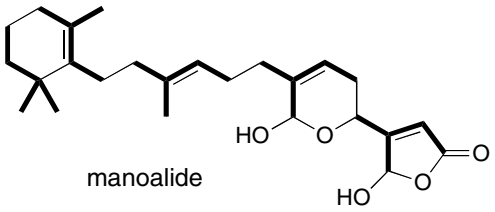


misoprostol
diastereomers
Only one tetrahedral stereogenic center is different in these two compounds.

29.11 Isoprene units are shown in bold.

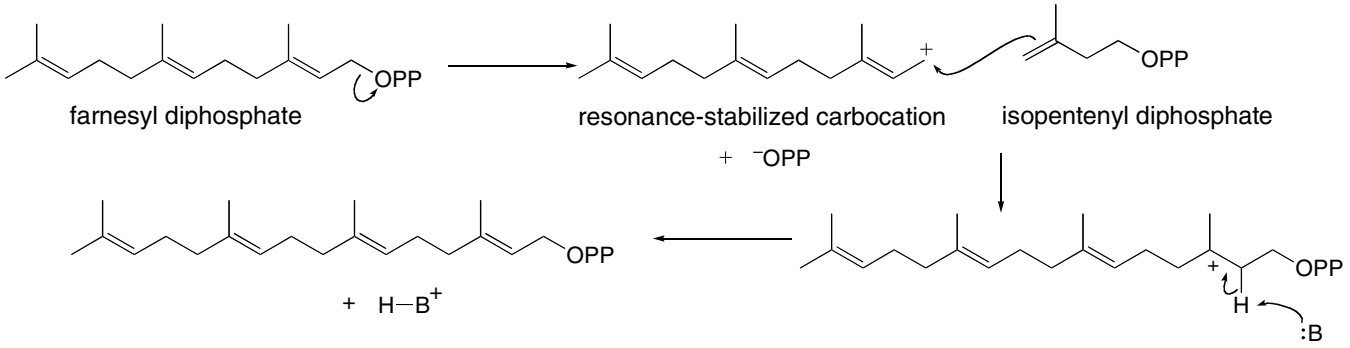


29.12

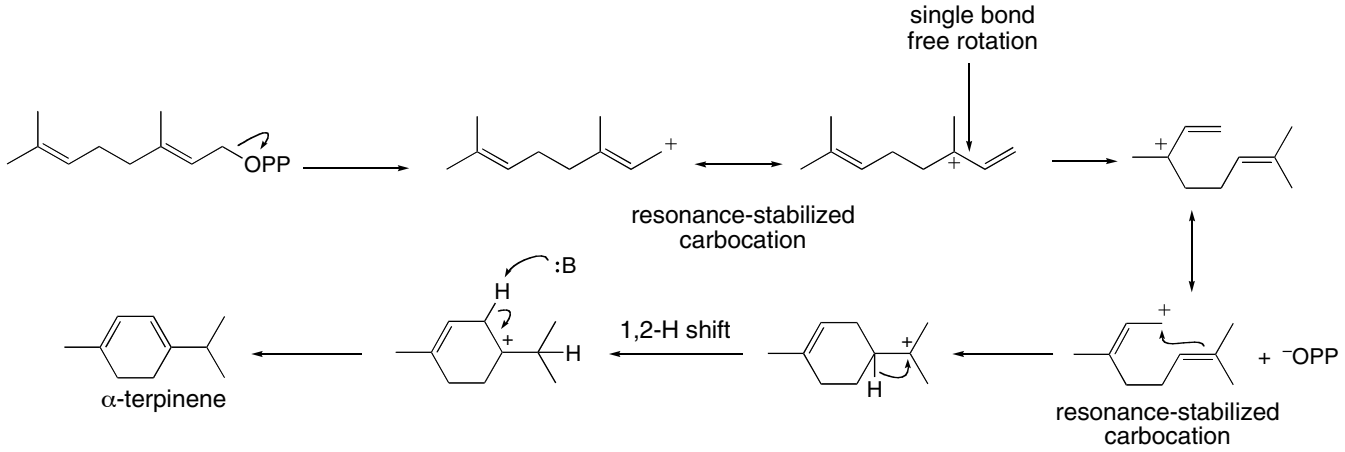


manoalide

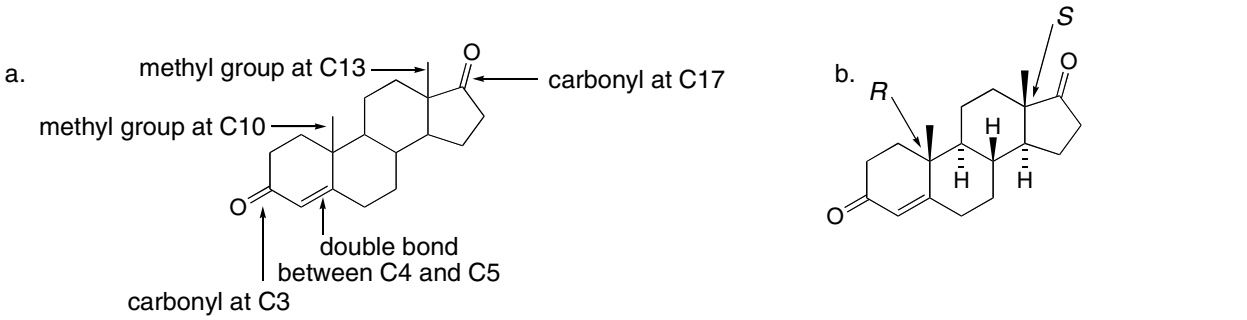
29.13



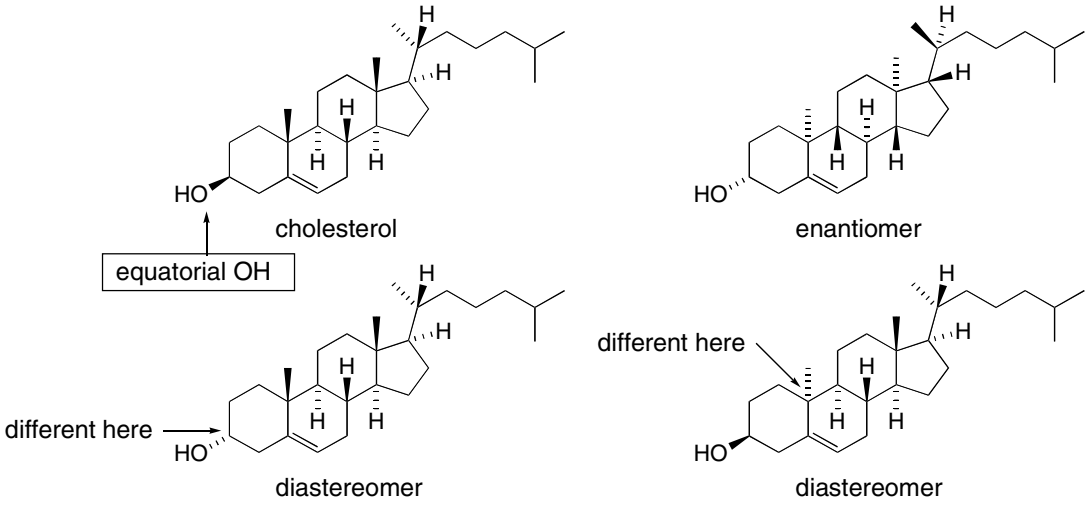
29.14



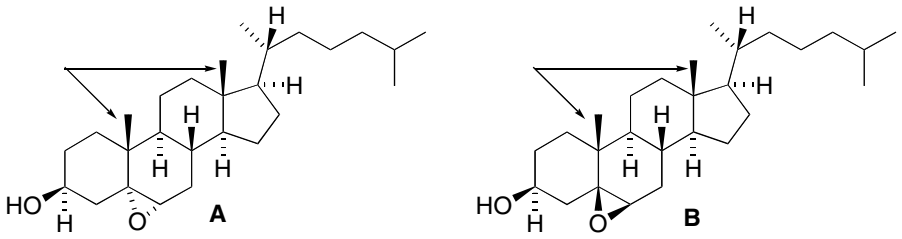
29.15



29.16

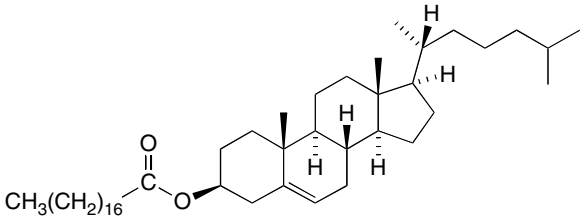


29.17

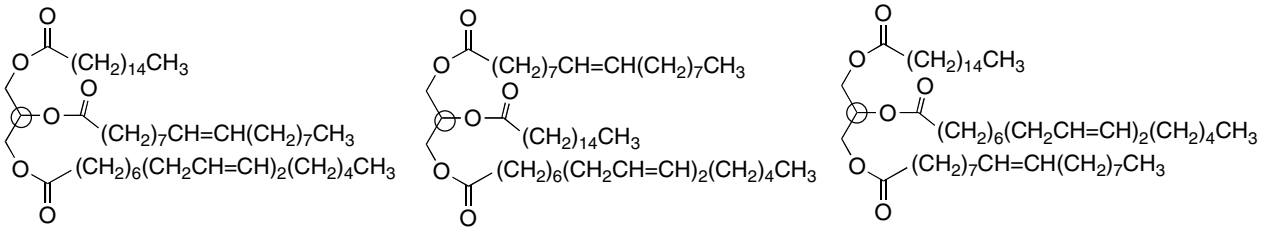


All four rings are in the same plane. The bulky CH_3 groups (arrows) are located above the plane. Epoxide **A** is favored, because it results from epoxidation below the plane, on the opposite side from the CH_3 groups that shield the top of the molecule somewhat to attack by reagents. In **B**, the epoxide ring is above the plane on the same side as the CH_3 groups. Formation of **B** would require epoxidation of the planar C=C from the less accessible, more sterically hindered side of the double bond. This path is thus disfavored.

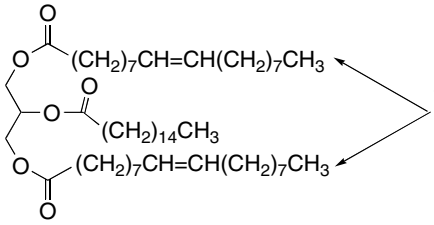
29.18



29.19 Each compound has one tetrahedral stereogenic center (circled), so there are two stereoisomers (two enantiomers) possible. All C=C's have the *Z* configuration.

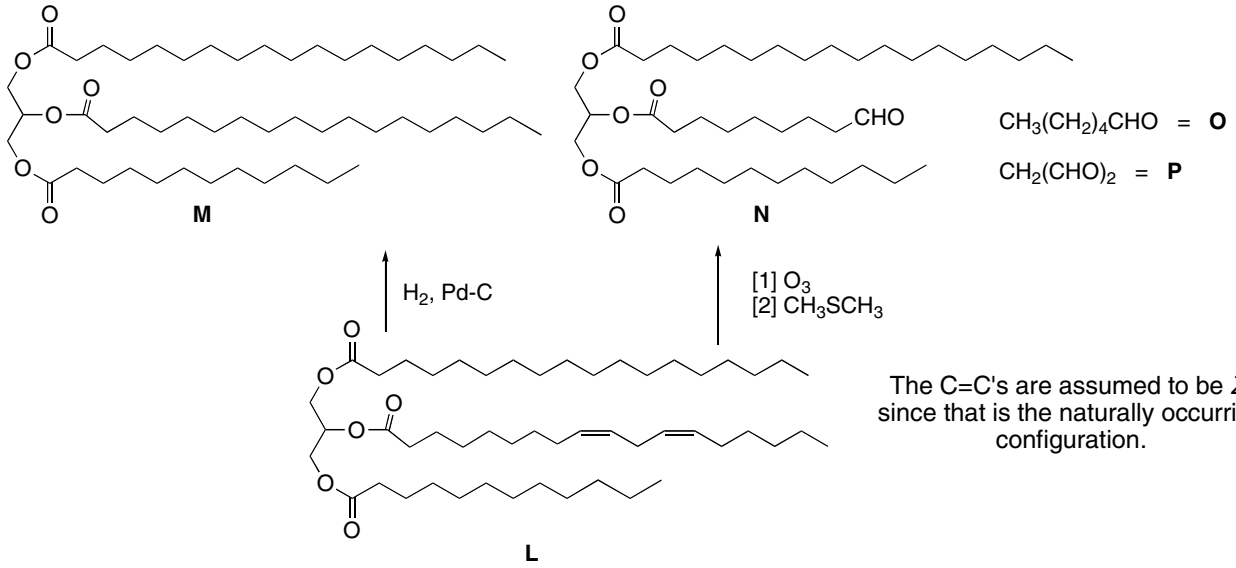


29.20



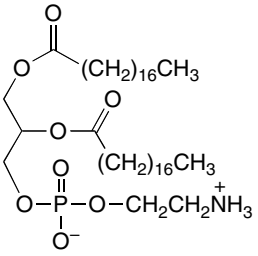
There is no stereogenic center in this triacylglycerol since these R groups are identical, making this triacylglycerol optically inactive.

29.21

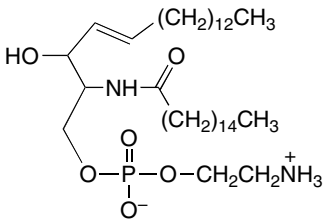


The C=C's are assumed to be *Z*, since that is the naturally occurring configuration.

29.22 When R" = $CH_2CH_2NH_3^+$, the compound is called a **phosphatidylethanolamine** or **cephalin.**



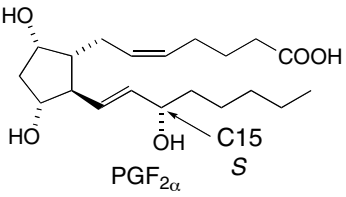
cephalin



sphingomyelin

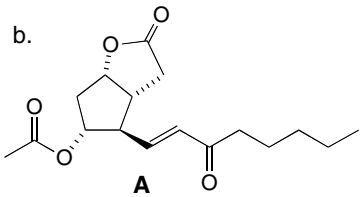
29.23

a.



$PGF_{2\alpha}$

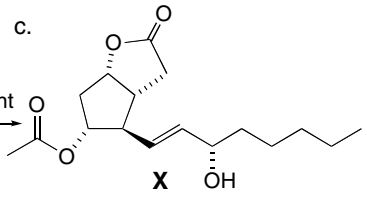
b.



A

[1] (*R*)-CBS reagent
[2] H_2O

c.

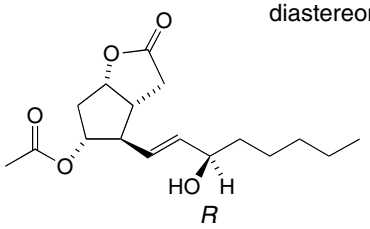


X

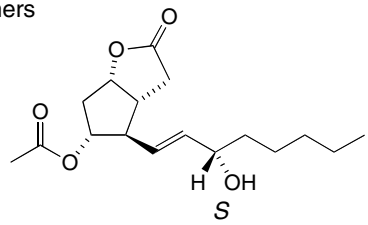
Use a chiral reducing agent to add hydride from one side only to form a single diastereomer.

[1] $Zn(BH_4)_2$
[2] H_2O

B and **C** diastereomers



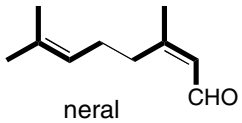
R



S

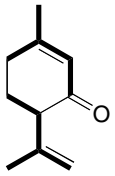
29.24

a.



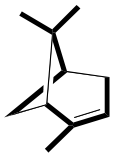
neral

b.



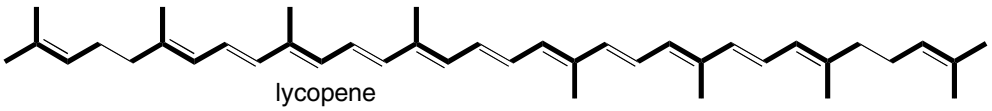
carvone

c.



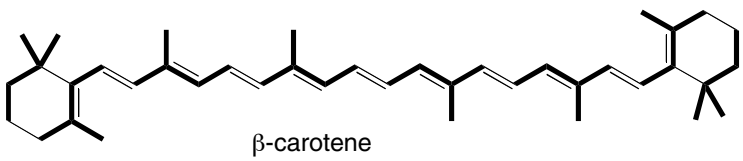
α-pinene

d.

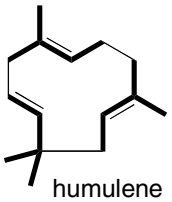


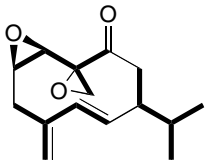
lycopene

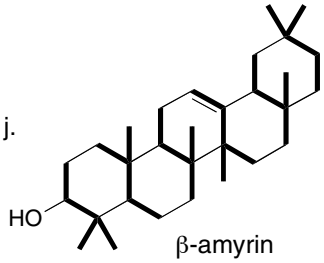
e.

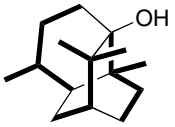


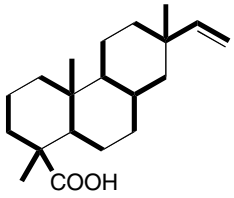
β-carotene

f. 
humulene

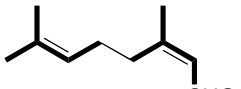
h. 
periplanone B

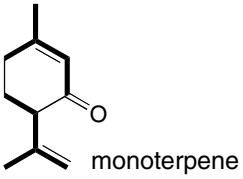
j. 
β-amyrin

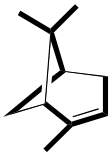
g. 
patchouli alcohol

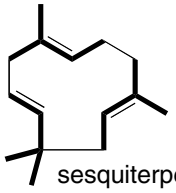
i. 
dextropimaric acid

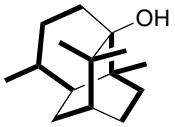
29.25 A ***monoterpene*** **contains 10 carbons** and two isoprene units; a ***sesquiterpene*** **contains 15 carbons** and three isoprene units, etc. See Table 29.5.

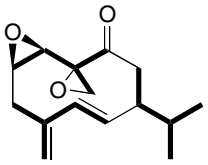
a. 
monoterpene

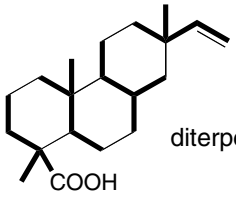
b. 
monoterpene

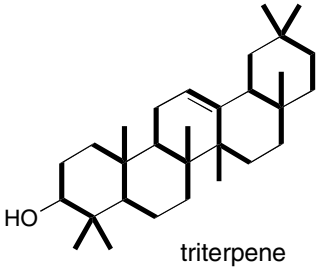
c. 
monoterpene

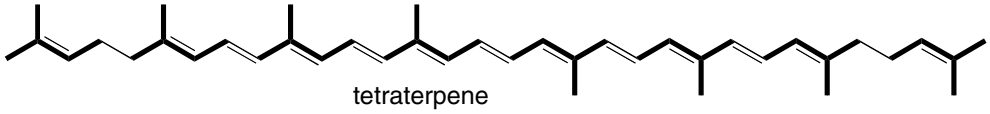
f. 
sesquiterpene

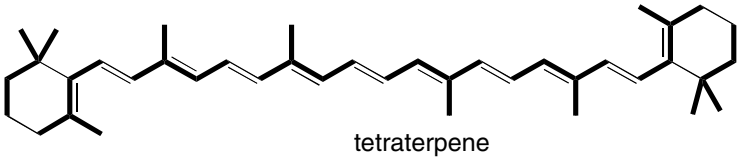
g. 
sesquiterpene

h. 
sesquiterpene

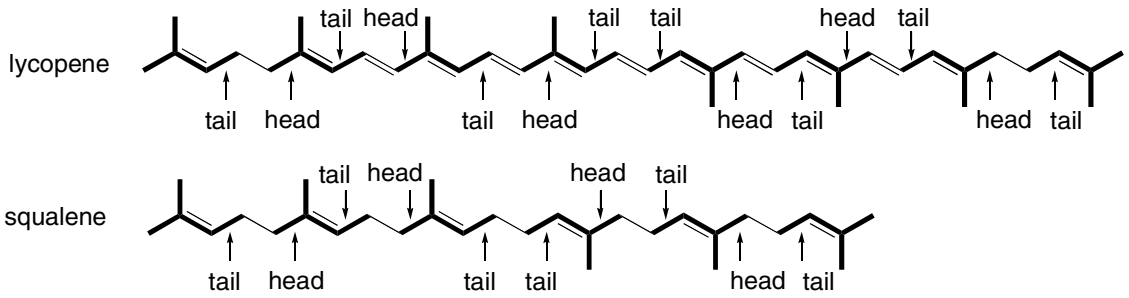
i. 
diterpene

j. 
triterpene

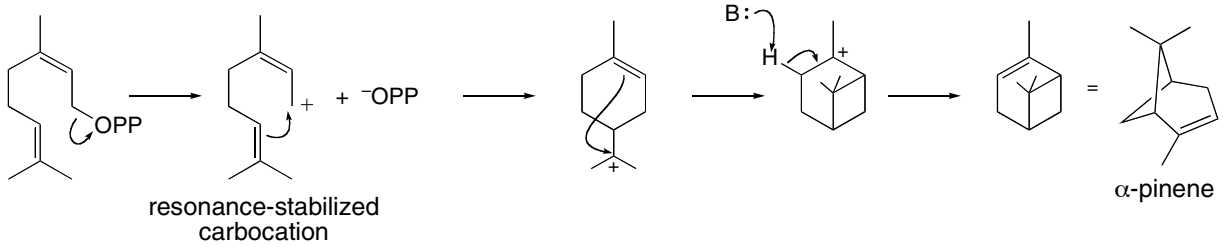
d. 
tetraterpene

e. 
tetraterpene

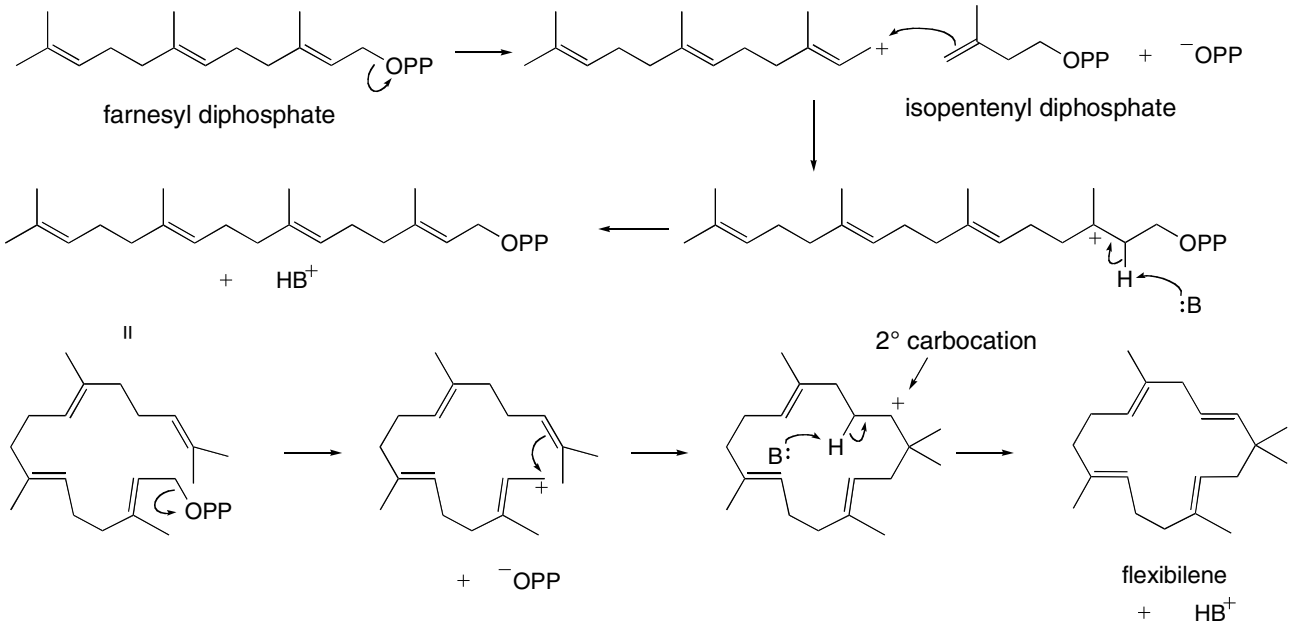
29.26



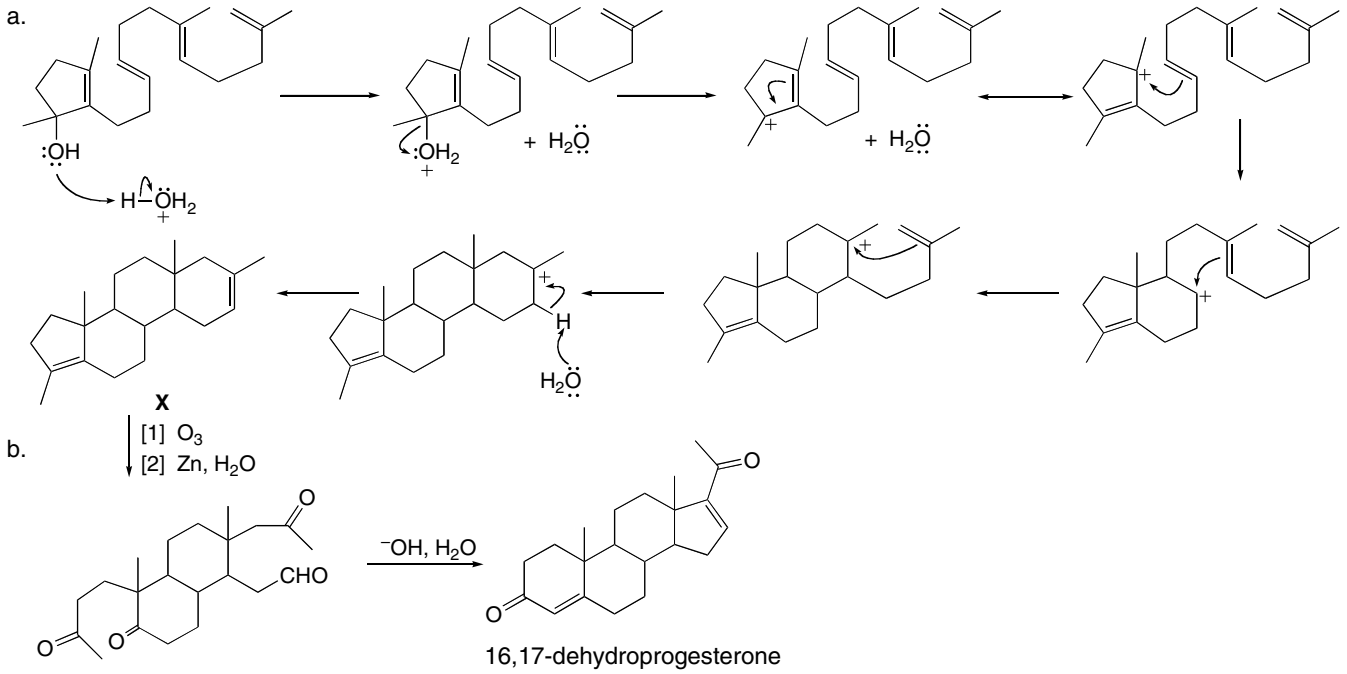
29.27



29.28 The unusual feature in the cyclization that forms flexibilene is that a 2° carbocation rather than a 3° carbocation is generated. Cyclization at the other end of the C=C would have given a 3° carbocation and formed a 14-membered ring. In addition, the 2° carbocation does not rearrange to form a 3° carbocation.

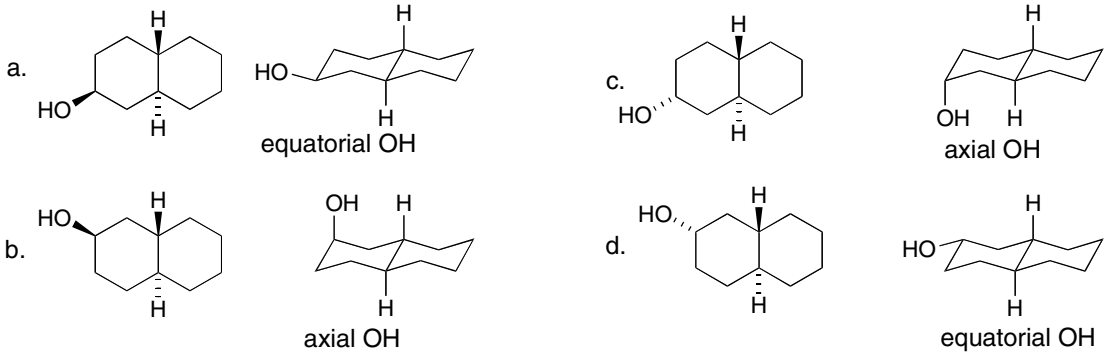


29.29

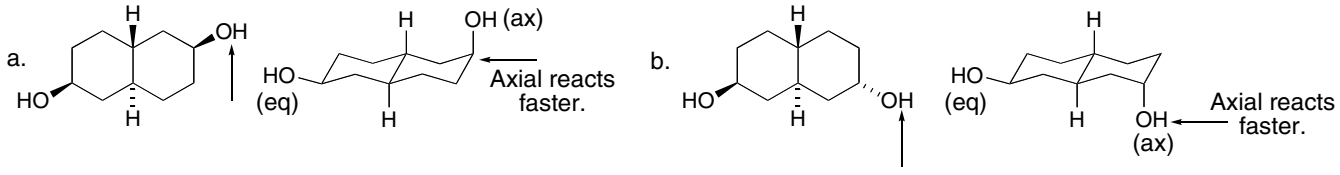


29.30

29.31

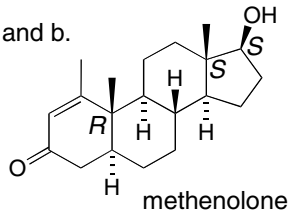


29.32



29.33

a. and b.

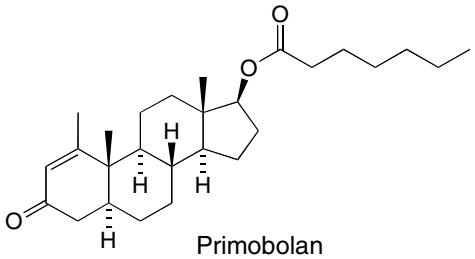


methenolone

c.

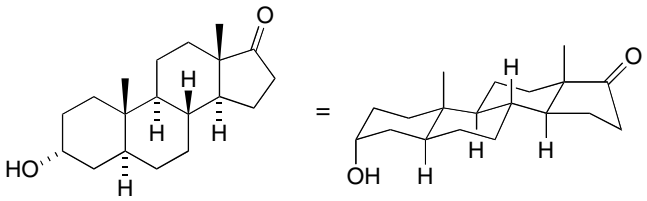
$CH_3(CH_2)_5COCl$

pyridine



Primobolan

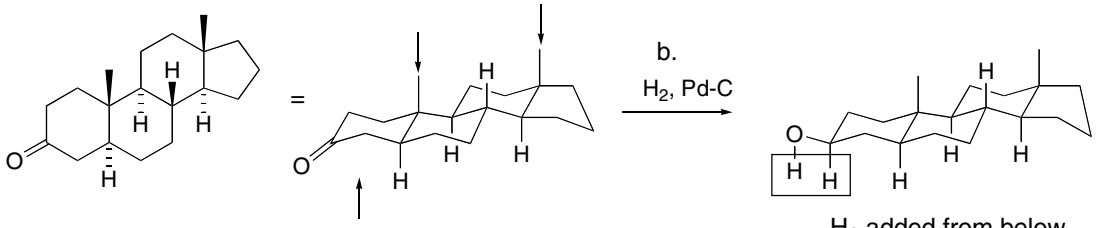
29.34



29.35

CH_3 groups make this face more sterically hindered.

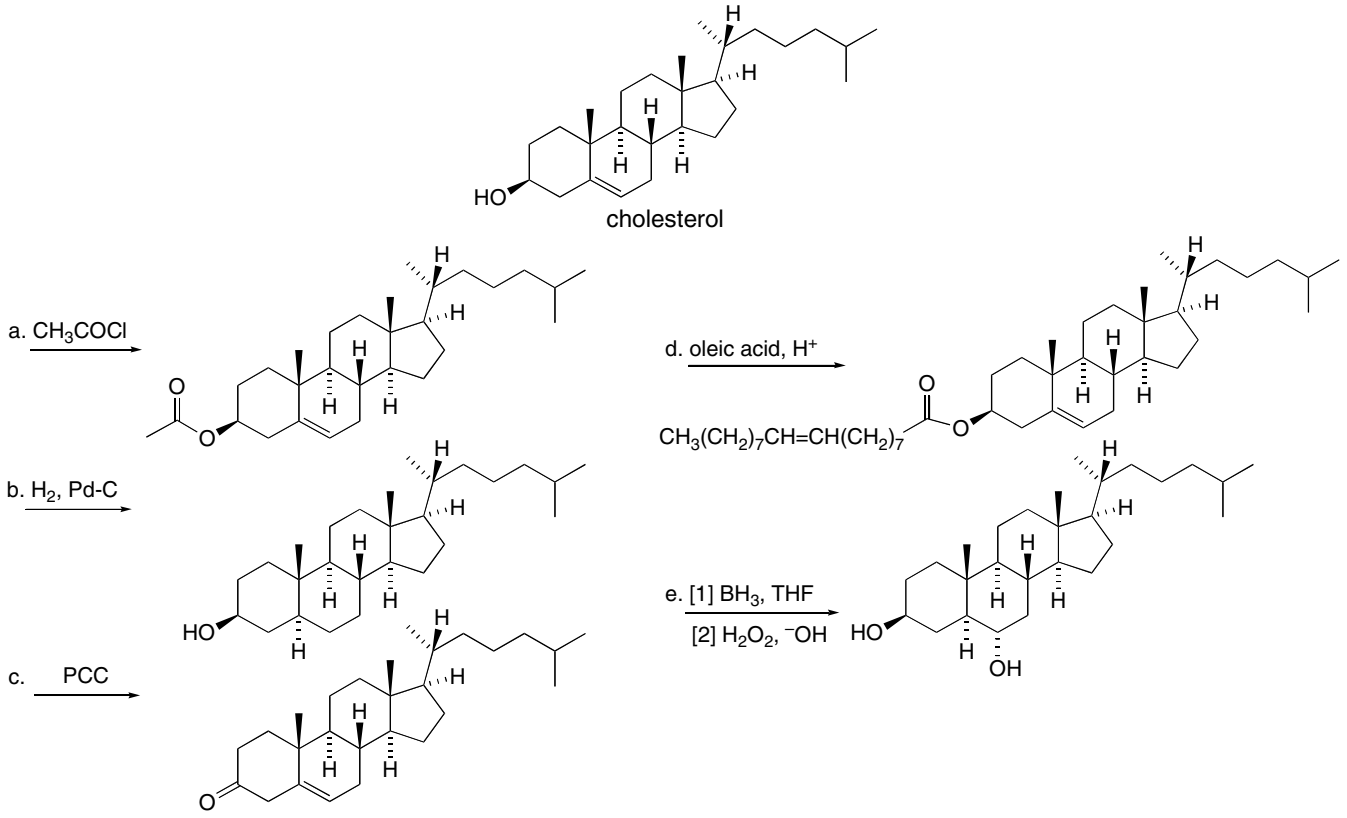
a.



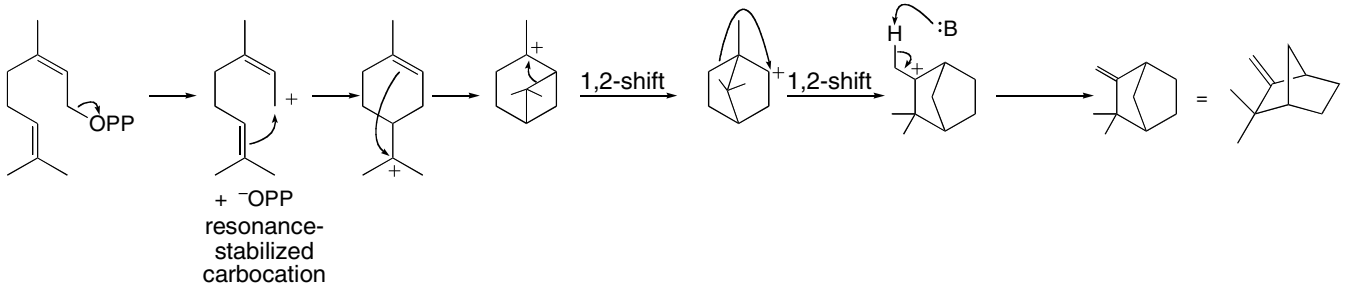
The bottom face is more accessible so the H_2 is added from this face to form an equatorial OH.

H_2 added from below

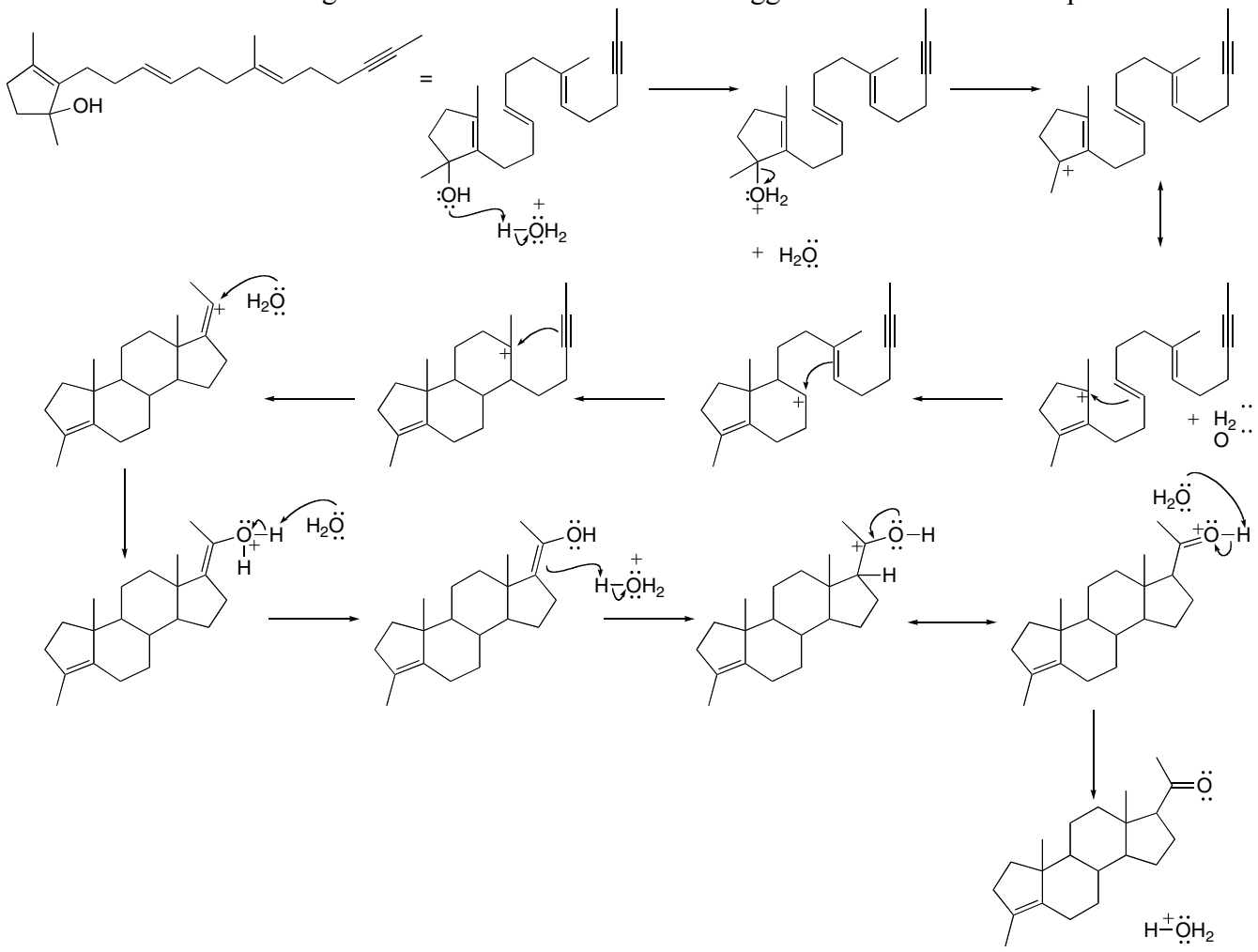
29.36


cholesterol
a. CH_3COCl
b. H_2, Pd-C
c. PCC
d. oleic acid, H^+
$CH_3(CH_2)_7CH{=}CH(CH_2)_7$
e. [1] BH_3, THF
[2] H_2O_2, ^-OH

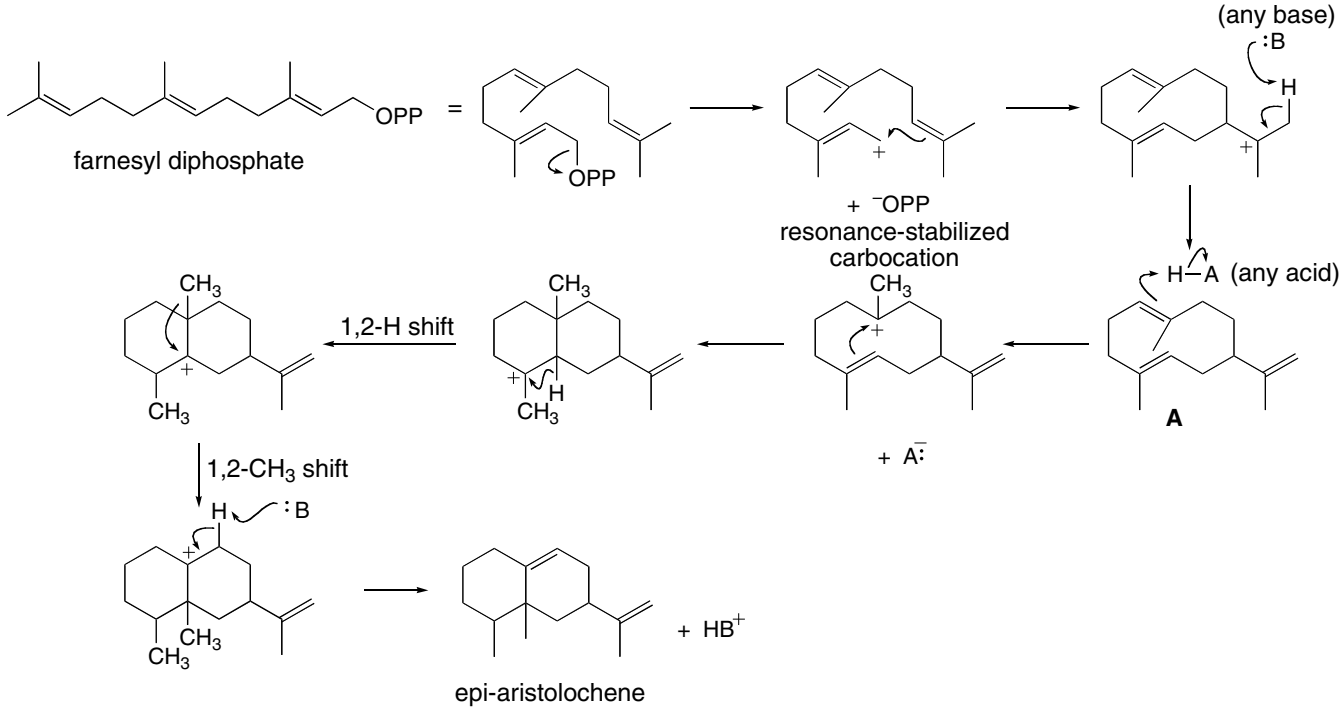
29.37


OPP
+ $^-$OPP
resonance-stabilized carbocation
1,2-shift
1,2-shift
H
:B
=

29.38 Re-draw the starting material in a conformation that suggests the structure of the product.



29.39


OPP
farnesyl diphosphate
=
OPP
+ ⁻OPP
resonance-stabilized
carbocation
(any base)
:B
H
H–A (any acid)
A
+ A:⁻
CH3
1,2-H shift
H
CH3
1,2-CH3 shift
:B
+ HB+
epi-aristolochene