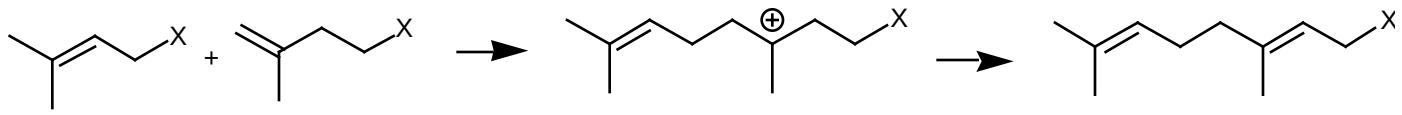
Chemistry 304B, Spring 1999 **Lecture 7**

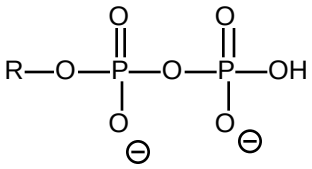
From last time:

The biosynthesis of polyisoprenoids: how make carbon-carbon bonds?
S_N2 with carbon nucleophile; leaving group?
Needs to work under physiological conditions: water, pH 6-8, 37 ºC



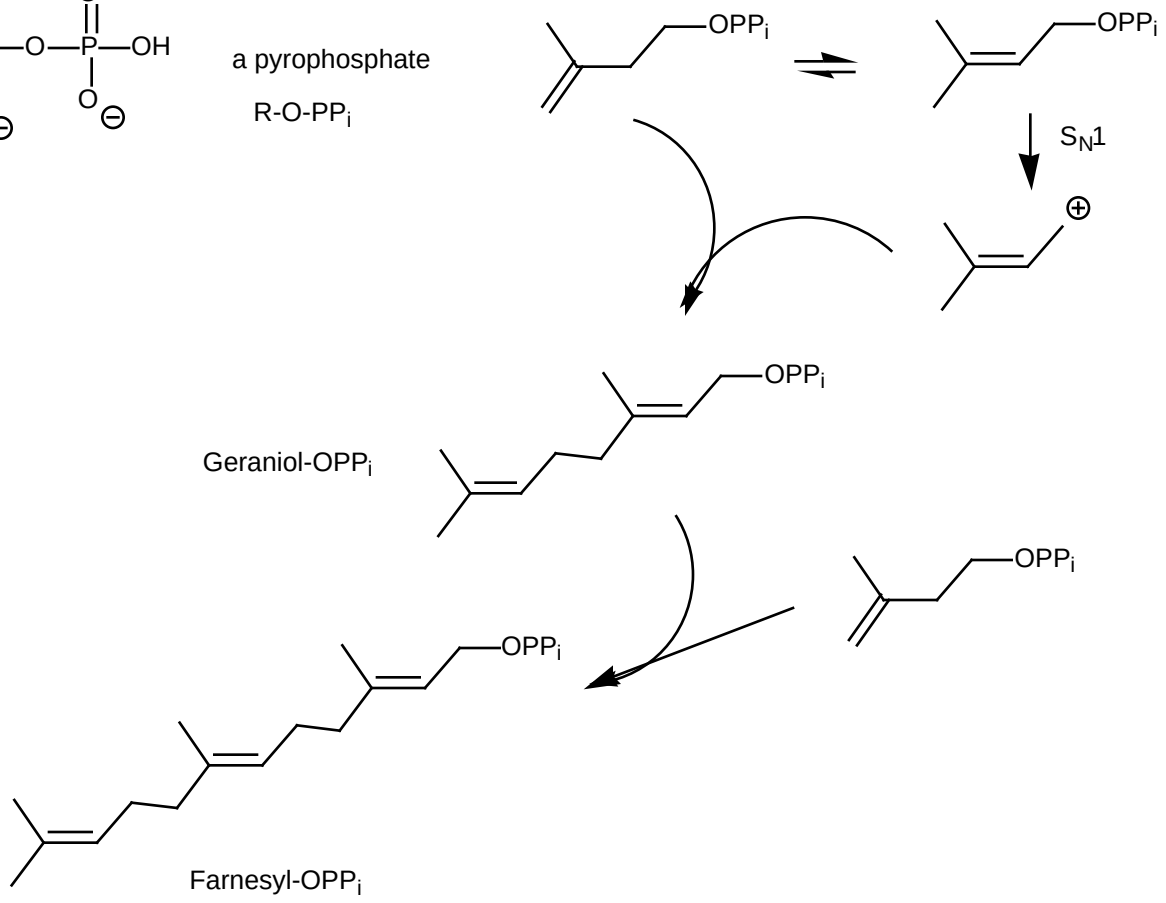
γ,γ-dimethylallyl-X isopentenyl-X

Nature's leaving group: pyrophosphate

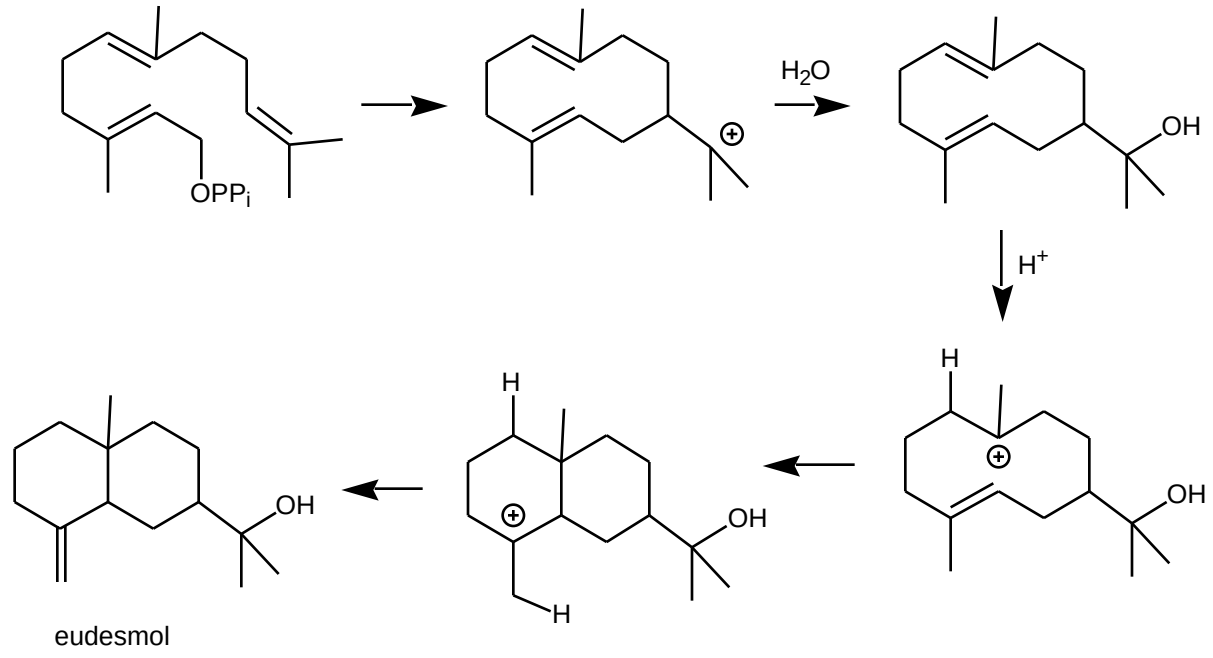


a pyrophosphate

R-O-PP_i



How form rings? Consider eudesmol.



eudesmol

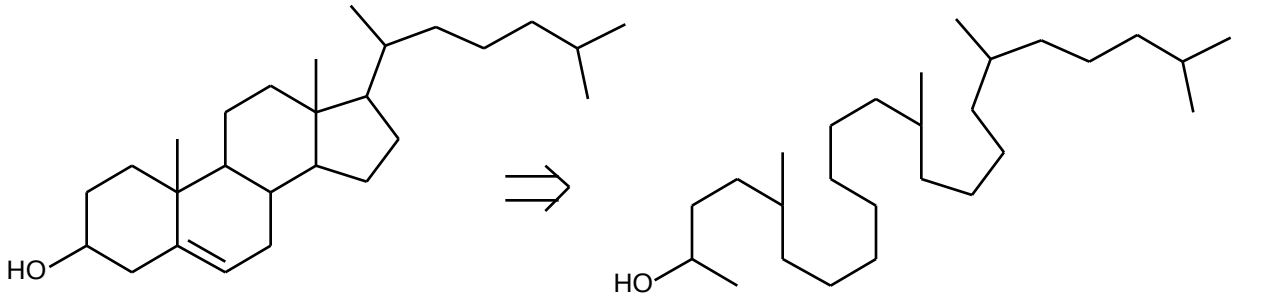
Can ionize allyl-OPP$_i$ to generate allylic cation

Cannot ionize any other -OPP$_i$ (e.g., primary, secondary, etc) or other leaving group.

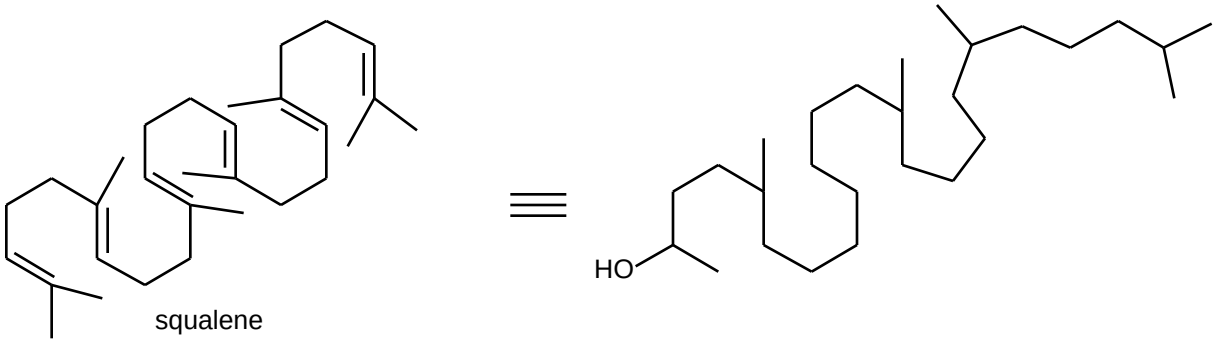
Can add a proton to a double bond to get a secondary or tertiary cation

Alkenes add to cations to give C-C bond and new cation.

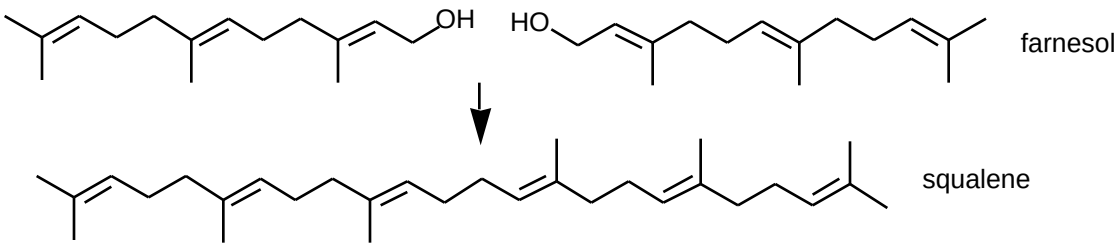
Note: cholesterol has some similarity to polyisoprenoids:

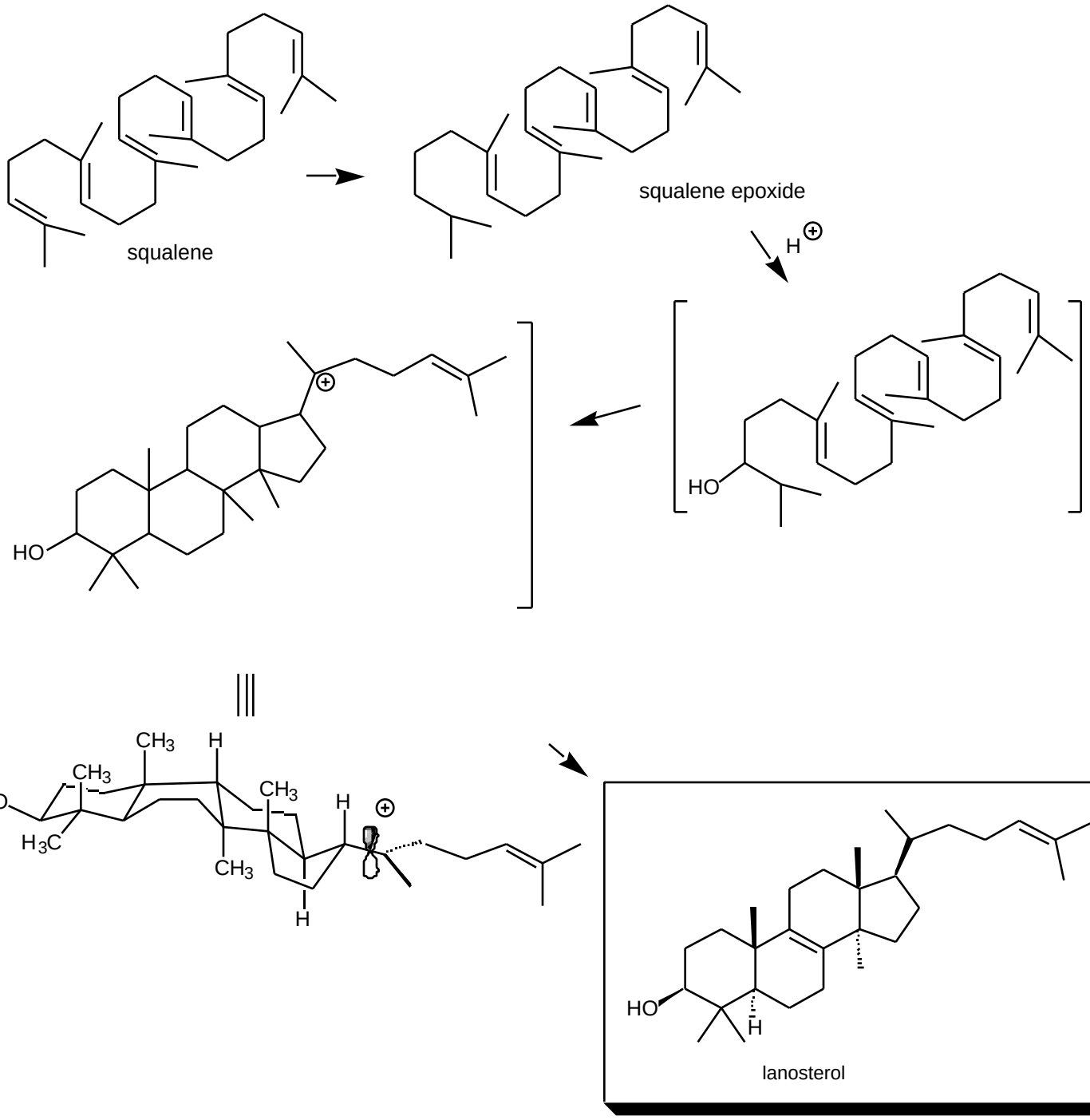


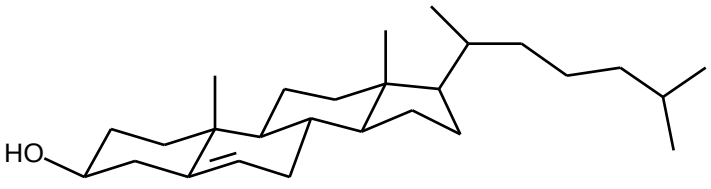
27 carbons
(3 have been removed)

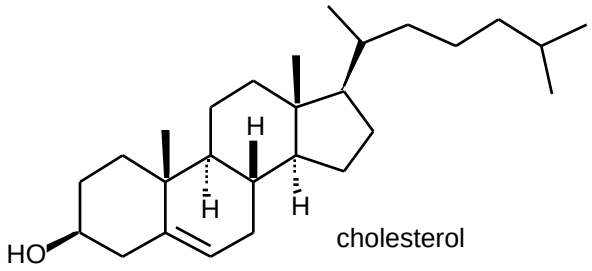


squalene

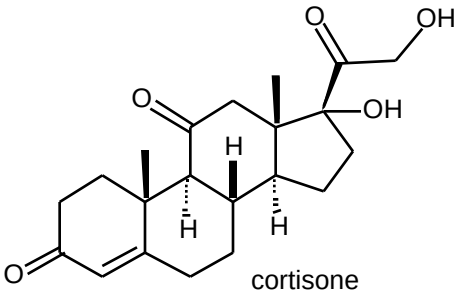

OH
HO
farnesol
squalene


squalene
squalene epoxide
H
HO
HO
CH3
H
CH3
HO
H3C
CH3
CH3
H
H
HO
H
lanosterol

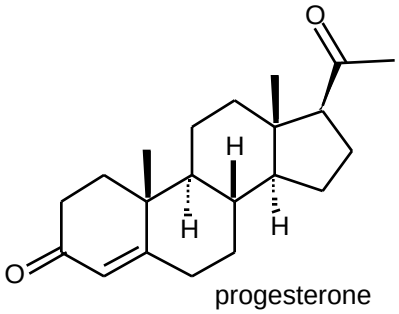




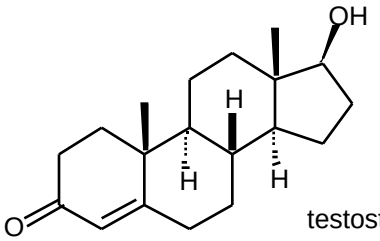
cholesterol



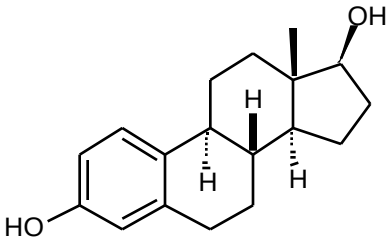
cortisone



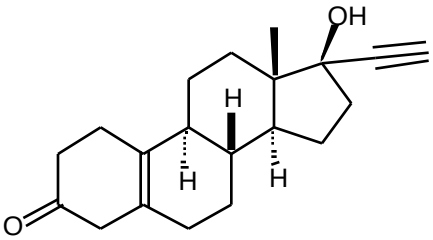
progesterone



testosterone

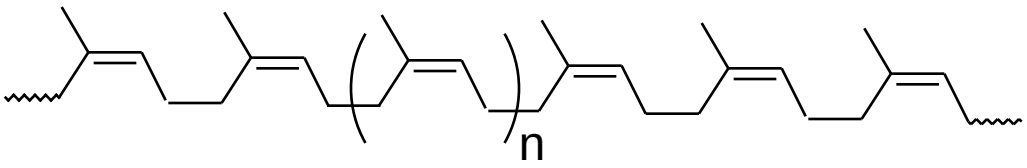


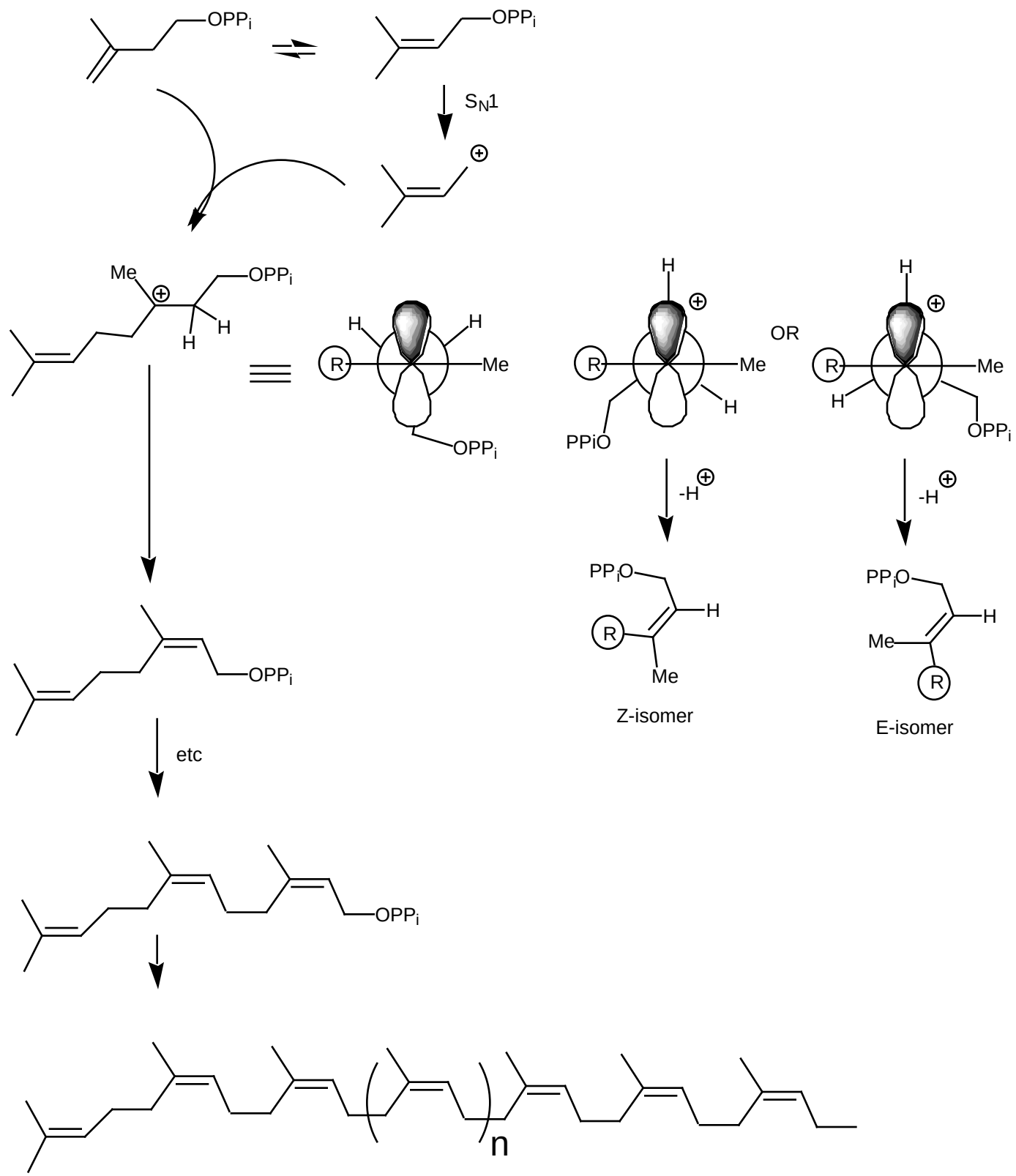
estradiol



norethynodrel

Natural Rubber:




OPPi
OPPi
SN1
Me
OPPi
H
H
H
≡
R
H
H
Me
OPPi
H
R
Me
H
PPiO
OR
H
R
Me
H
OPPi
-H
-H
PPiO
R
H
Me
PPiO
H
Me
R
Z-isomer
E-isomer
OPPi
etc
OPPi
n