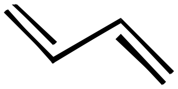
Chemistry 304B, Spring 1999 Lecture 6

From last time:

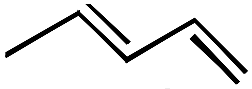
Lengthening the string of p orbitals (e.g, ethylene to 1,3-butadiene) narrows the HOMO-LUMO gap and gives rise to UV absorption at longer wavelengths, lower energy, for the $\pi-\pi$ excitation. This is a regular and fairly predictable phenomenon, and adding one new pi bond increases λ for the lowest energy absorption by about 30-35 nm. Functional groups in conjugation, such as the carbonyl group in retinal and in canthaxanthin, also change the $\pi-\pi$ gap, but not necessarily by the same magnitude as the addition of a simple alkene unit.

The intrinsic intensity of the absorption is a separate parameter, measured as the extinction coefficient, and is not easily correlated with structure, other than to say $\pi-\pi$ absorption is strong (ε 10,000-100,000) and $n-\pi$ absorption is weak (10-100). The position (λ_{max}) and the intensity (e) are independent and do not correlate with one another. I.e., it is not correct that longer λ absorption has higher ε.

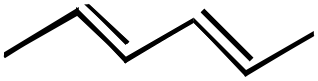
There are other structural correlations with UV absorption:



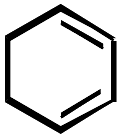
1,3-butadiene



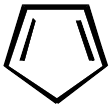
1,3-pentadiene



2,4-hexadiene

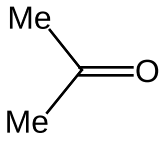


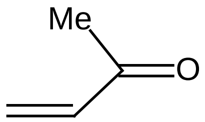
1,3-cyclohexadiene



1,3-cyclopentadiene

In a typical ketone, the MO distribution has a high lying pi orbital and a still higher energy set of non-bonding electrons (highest filled orbitals).





Summary:

UV spectroscopy is a detector of pi bonds; no pi bonds--no UV absorption

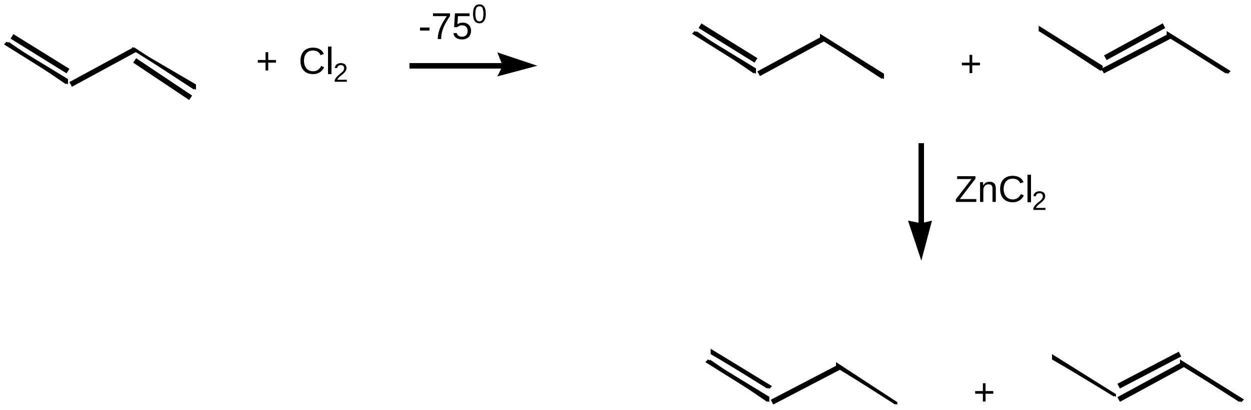
position of λ_{max} for longest $\lambda \rightarrow$ number of interacting p orbitals

intensity: low = $n \rightarrow \pi^*$ high = $\pi \rightarrow \pi$

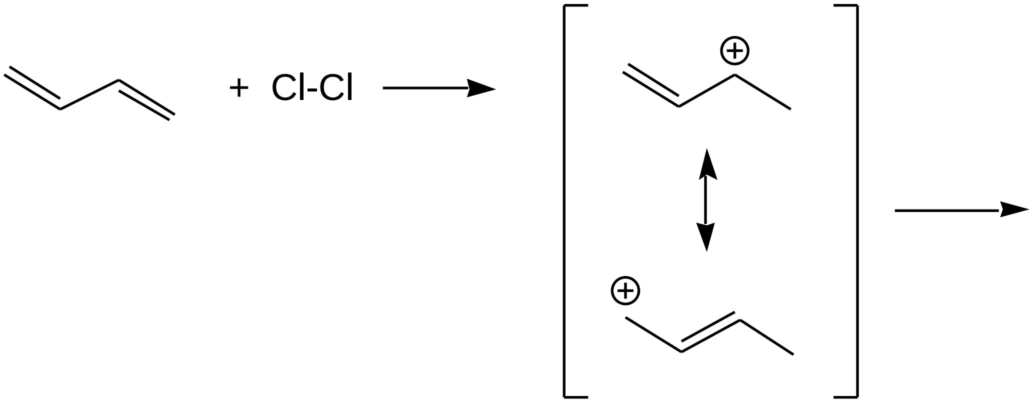
Reactions of 1,3-Dienes---What's special?

a. Reactions with electrophiles

Jones, Sec 12.8, 12.9, 12.10, 12.11, 12.12, 12.13, 12.14

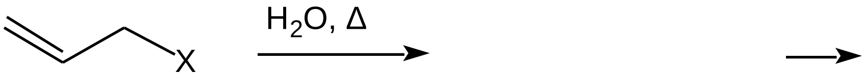


Mechanism:

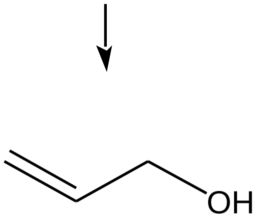


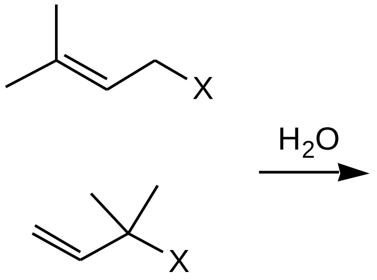
Same for H-Br, H-Cl, Br$_2$

The Allylic Cation also shows up in reactions of allyl halides and related derivatives

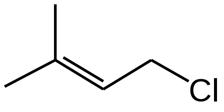


X = electronegative atom, leaving group

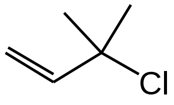




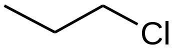
Note rates of reaction:



1.9×10^6



7.9×10^6



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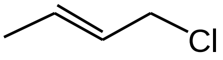
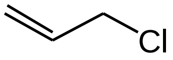


1.3×10^2

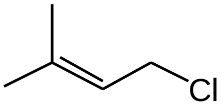


14.3

Note also: S_N2

S_N2 conditions--strong nucleophile

Reaction with NaOEt in EtOH



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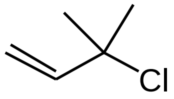
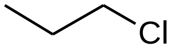


NA



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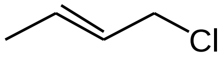

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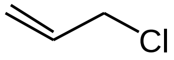

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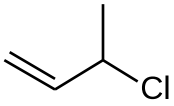
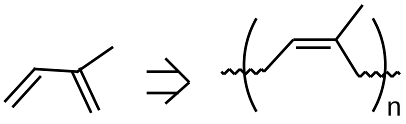


1.85

Biosynthesis: Where do β-carotene, retinol come from? **LIPIDS**

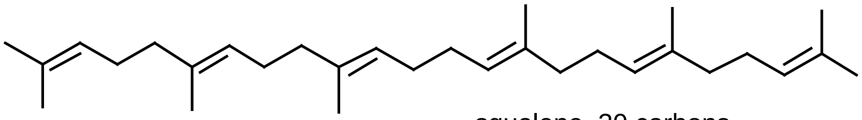
Fatty acids, steroids, vitamin A, etc.

Two main pathways: **two-carbon** → acetate
five-carbon → isoprene

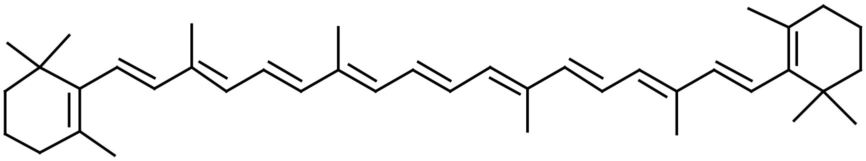


isoprene

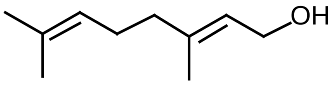
polyisoprene

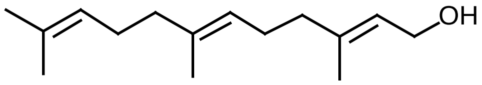


squalene, 30 carbons



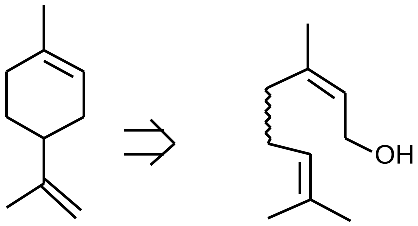
β-carotene, 40 carbons



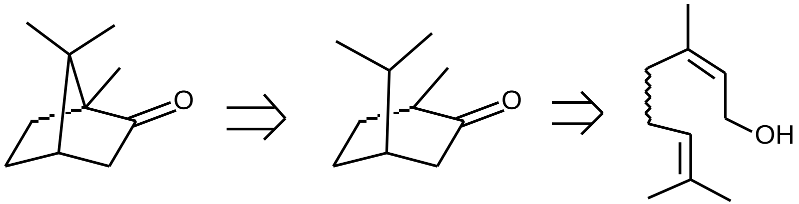


geraniol, 10 carbons

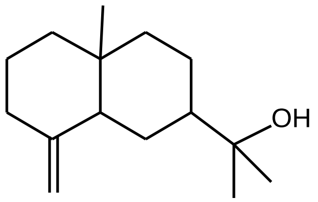
farnesol, 15 carbons



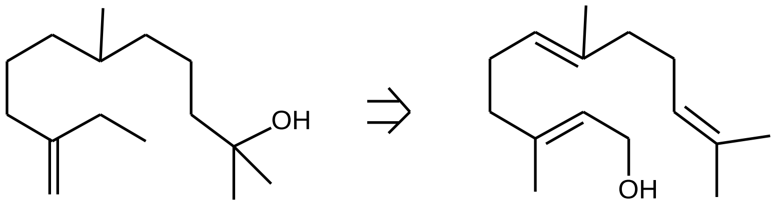
limonene



camphor

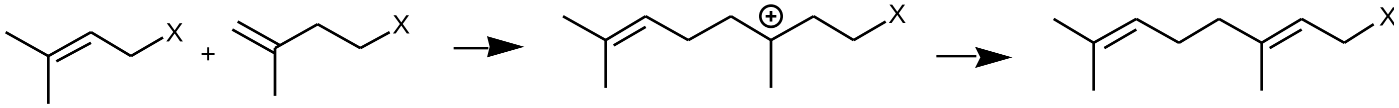


Eudesmol, from eucalyptus oil
15 carbons, a sesquiterpene



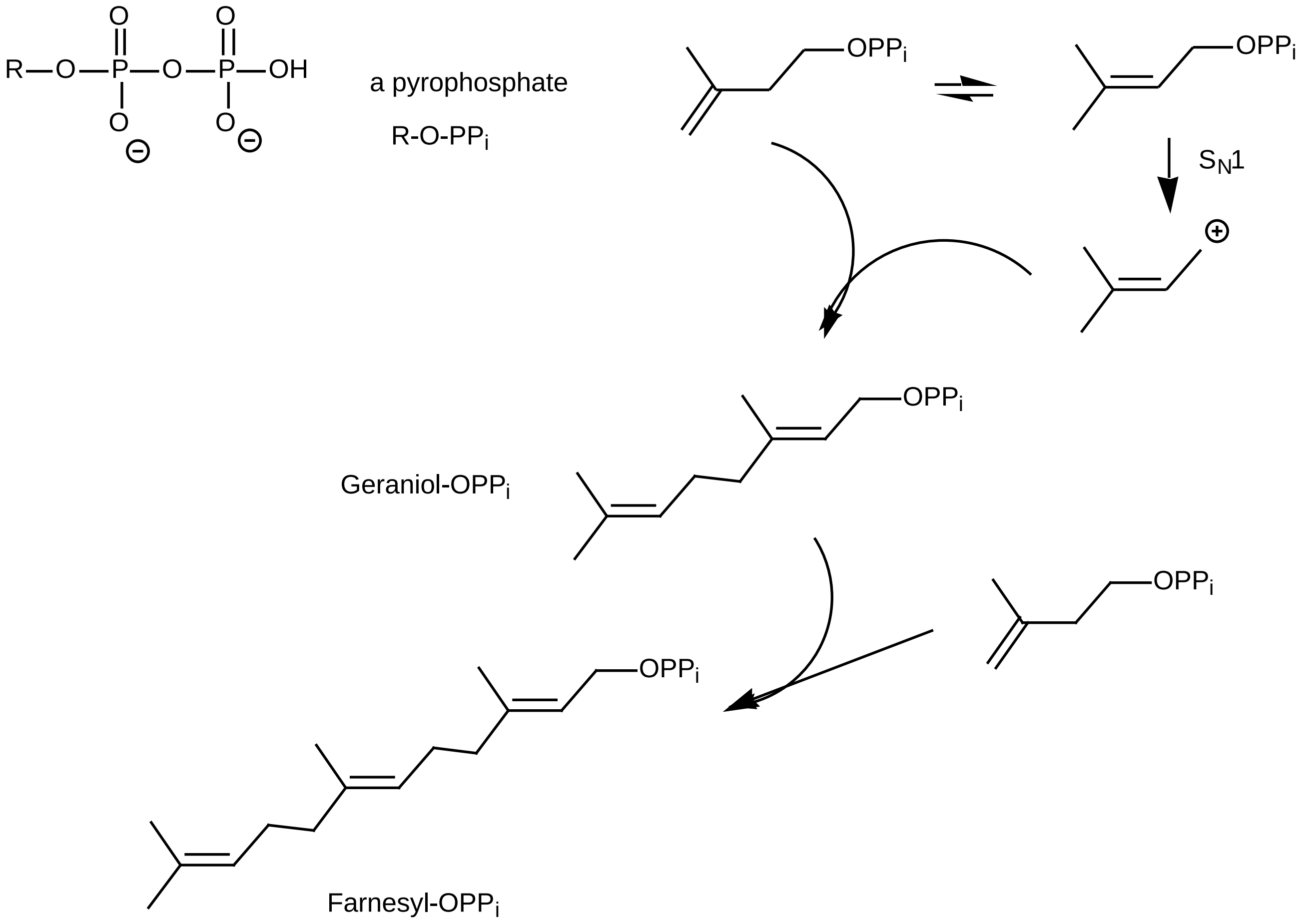
farnesol

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

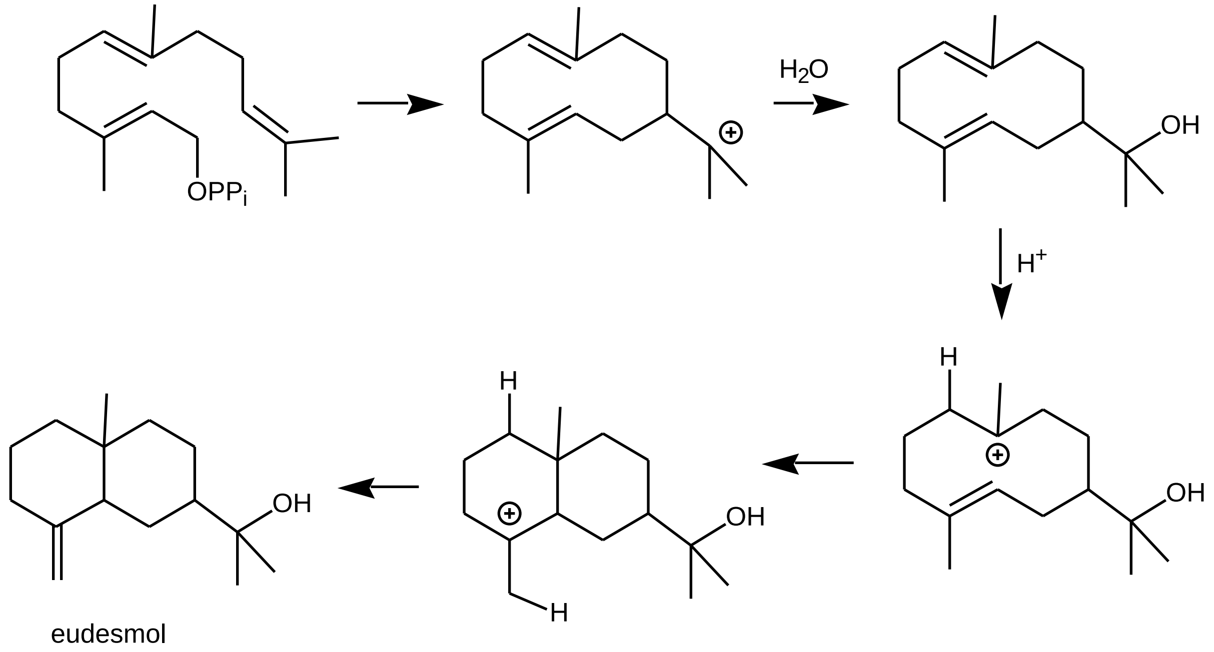


γ,γ-dimethylallyl-X isopentenyl-X

Nature's leaving group: pyrophosphate



How form rings? Consider eudesmol.



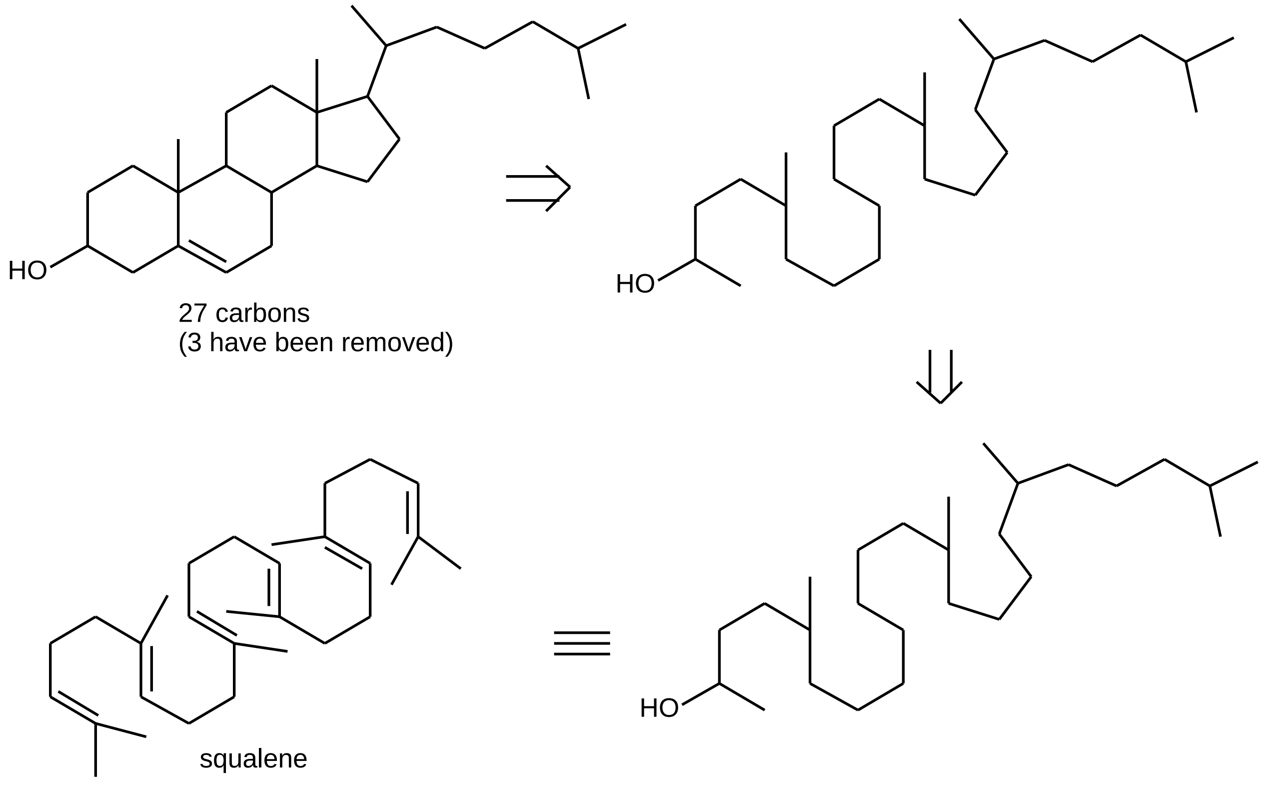
Can ionize allyl-OPP$_i$ to generate allylic cation

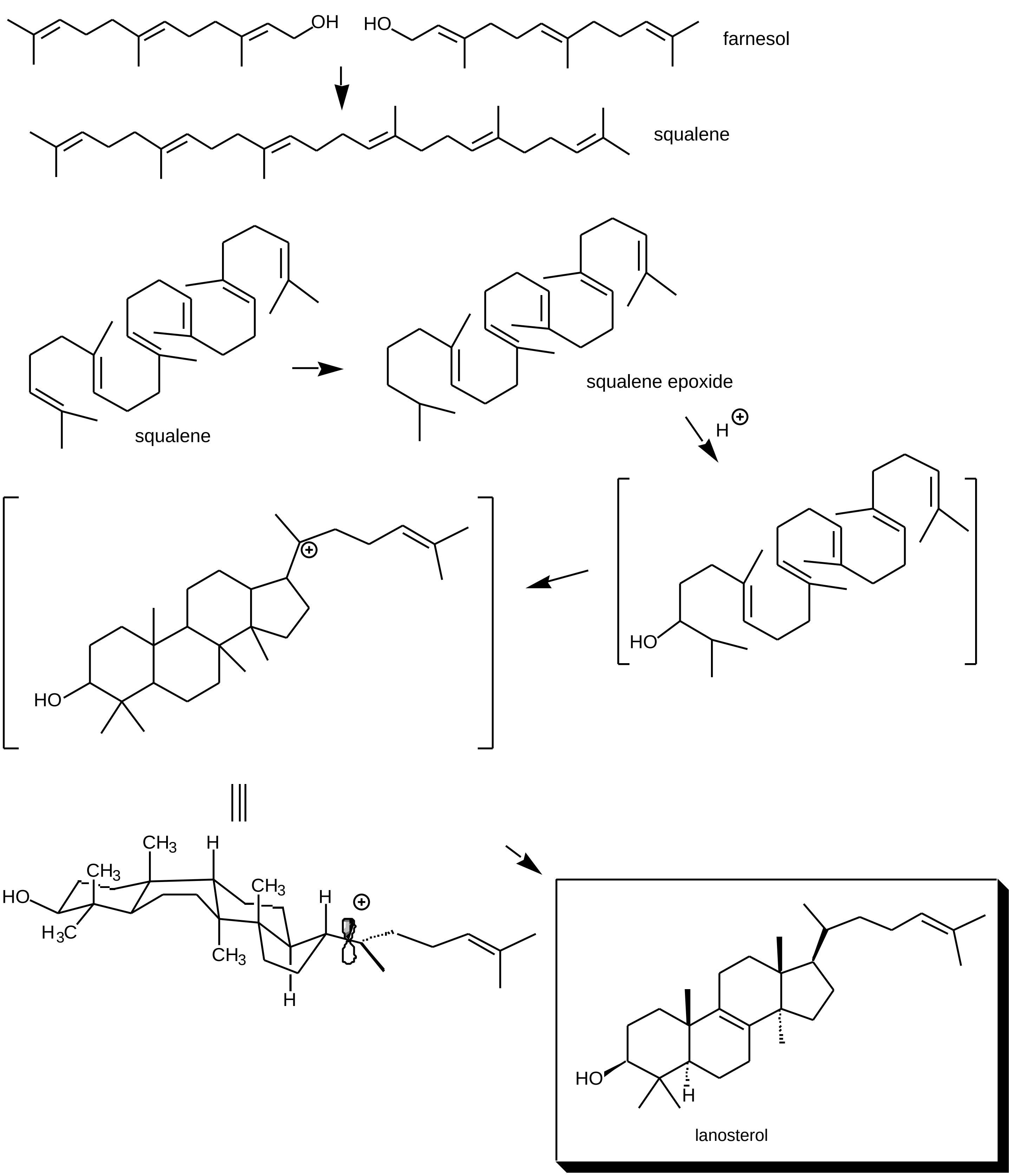
Cannot ionize any other -OPP$_i$ (e.g., primary, secondary, etc) or other leaving group.

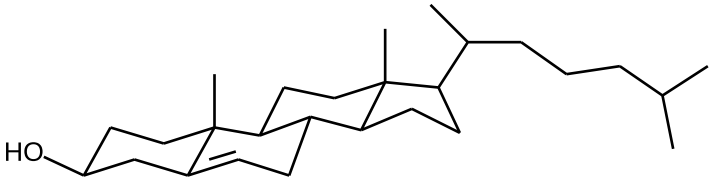
Can add a proton to a double bond to get a secondary or tertiary cation

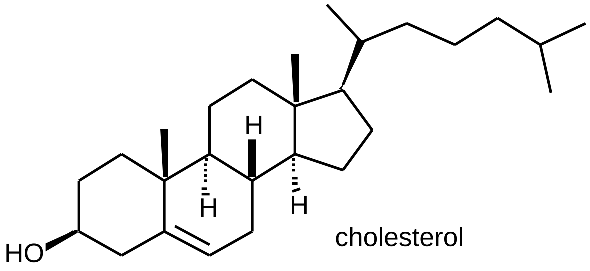
Alkenes add to cations to give C-C bond and new cation.

Note: cholesterol has some similarity to polyisoprenoids:

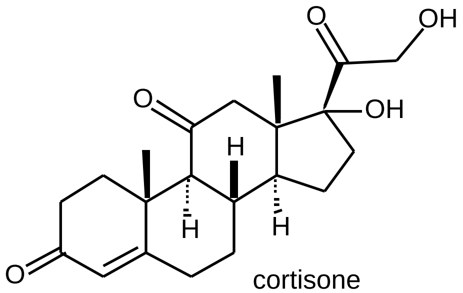



OH
HO
farnesol
squalene
squalene
squalene epoxide
H ⊕
HO
HO
⊕
CH3
H
CH3
CH3
HO
H3C
CH3
H
⊕
H
HO
H
lanosterol

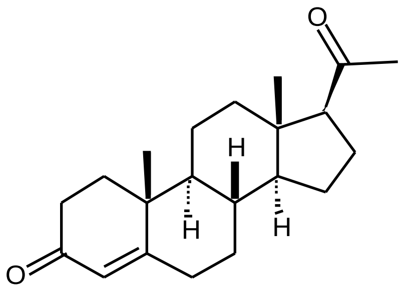




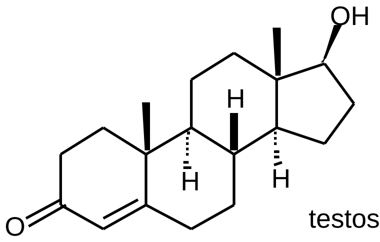
cholesterol



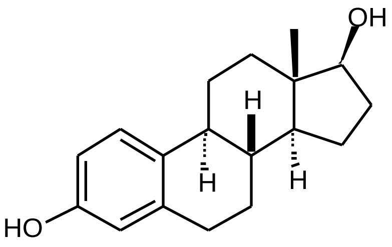
cortisone



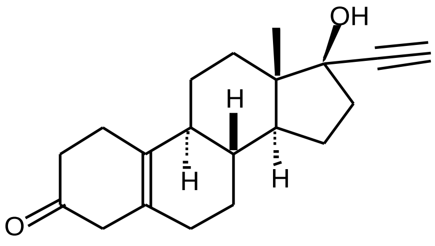
progesterone



testosterone

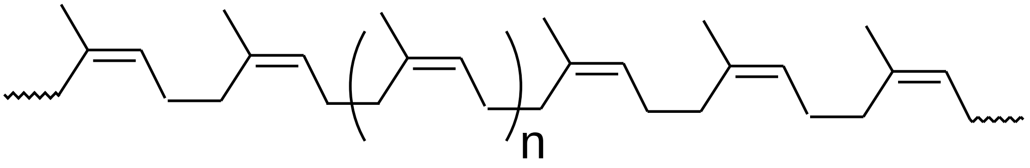


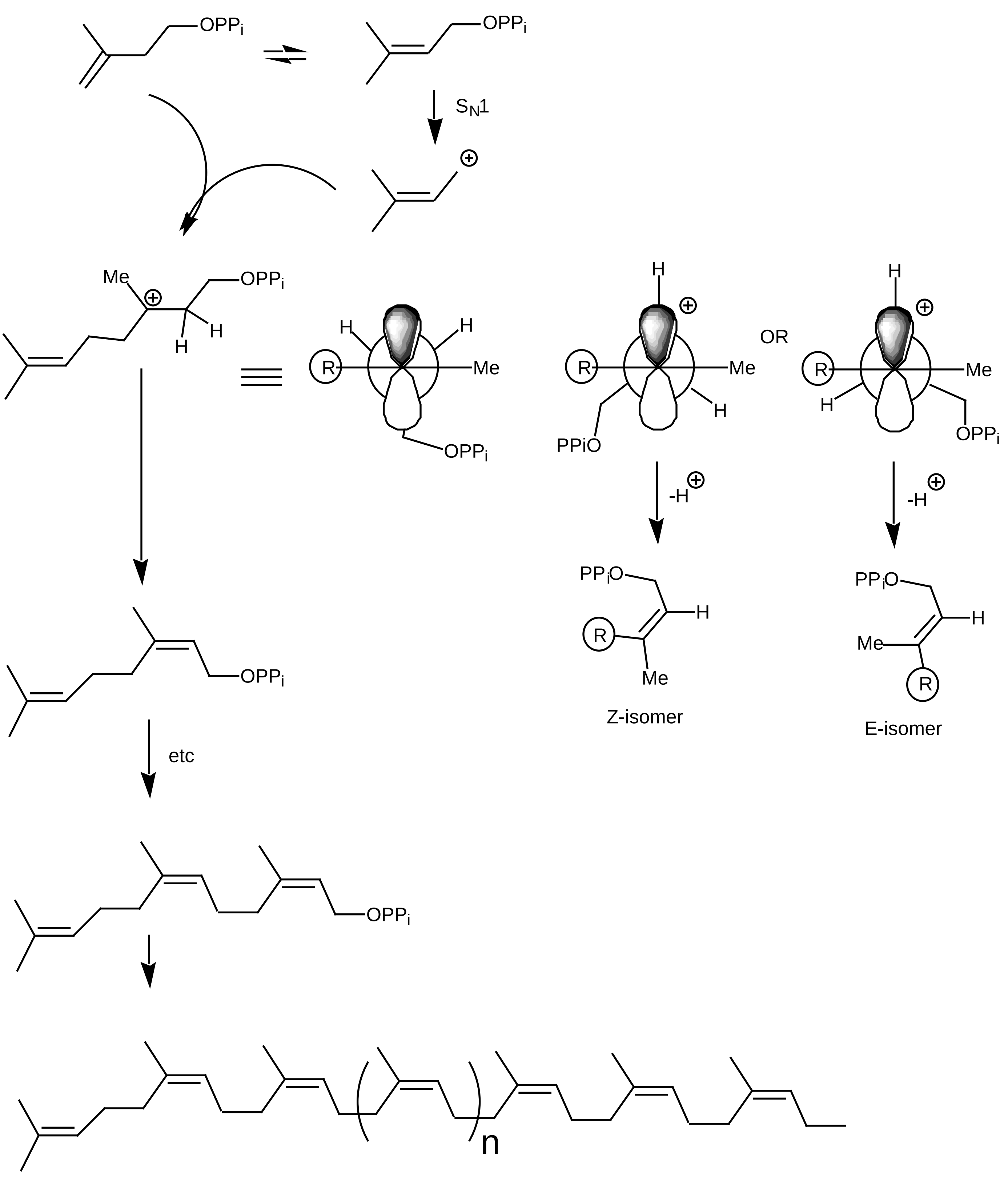
estradiol



norethynodrel

Natural Rubber:




OPP$_i$
OPP$_i$
S$_N$1
Me
OPP$_i$
H
H
H
H
R
Me
OPP$_i$
H
R
Me
PPiO
H
OR
H
R
Me
H
OPP$_i$
-H
-H
PP$_i$O
H
R
Me
Z-isomer
PP$_i$O
H
Me
R
E-isomer
OPP$_i$
etc
OPP$_i$
n