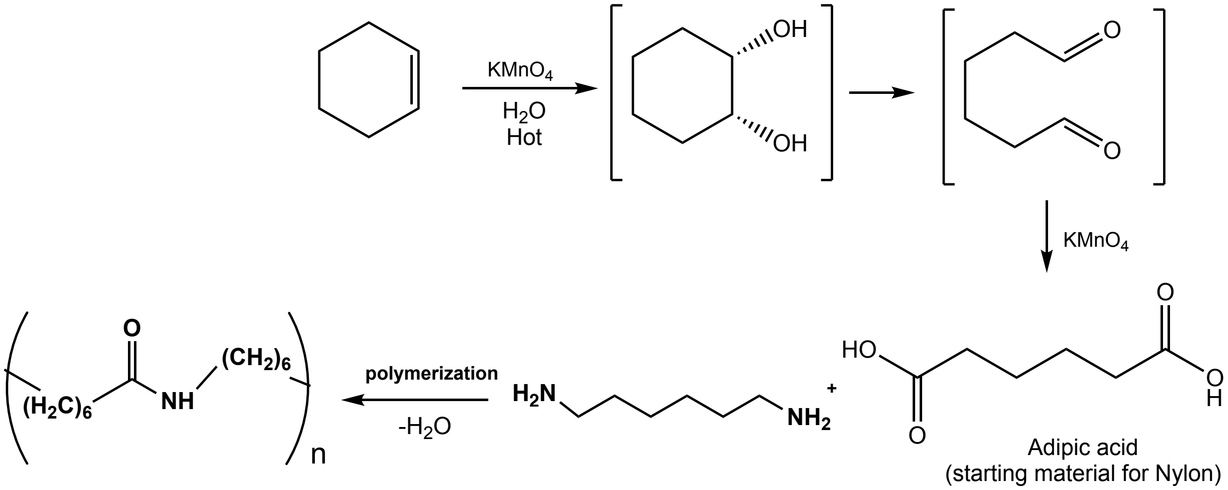
Review

When tackling a mechanism, always ask yourself two things:

- Where are the electrons going?
- What functional groups are added or removed?

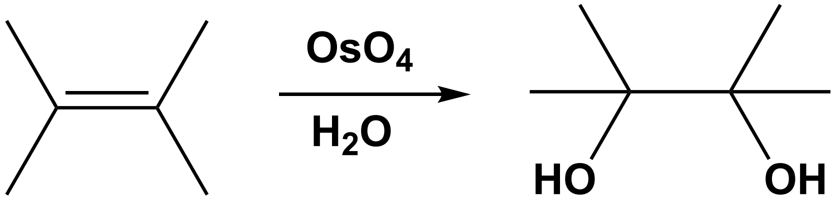
From the last week's example 5



Electrons? Oxidation – electron loss (organic compound)
Functional Groups? Dihydroxylation – two hydroxyl groups (OH) are added

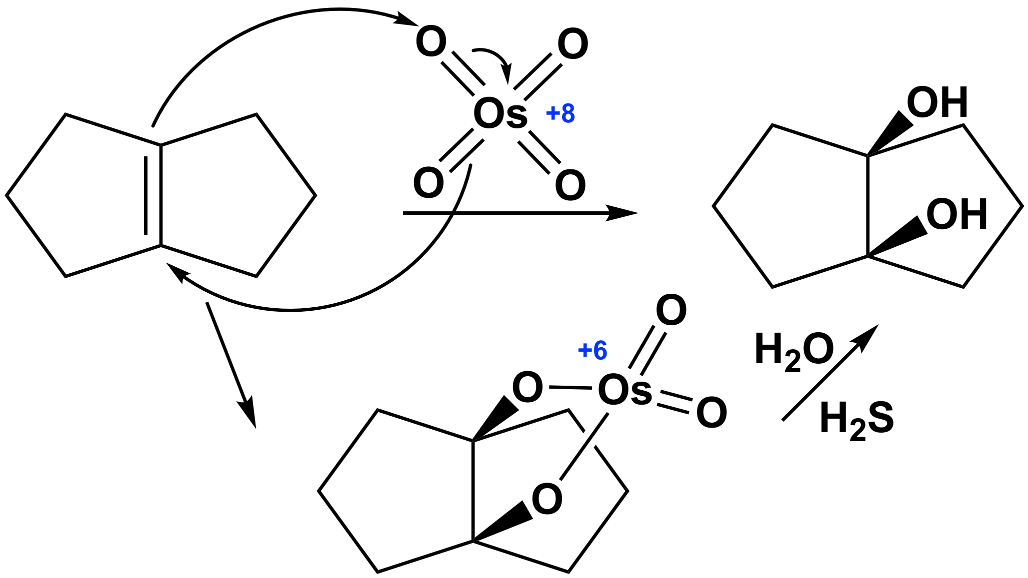
Dihydroxylation with OsO_4

General Scheme



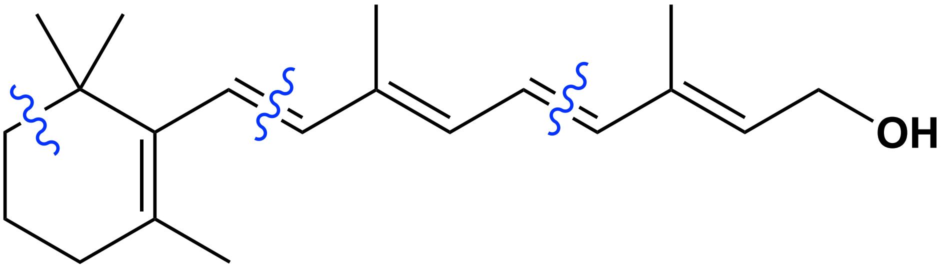
Unlike MnO_4, this is a *chemo-selective* reaction and just the dihydroxylation occurs; there is no further oxidation

Example 1



OsO_4 – volatile (high vapour pressure, and can easily be inhaled)
If inhaled, it can make you blind. *Why?*

The molecule required for vision:



Retinol (opsin → rhodopsin)

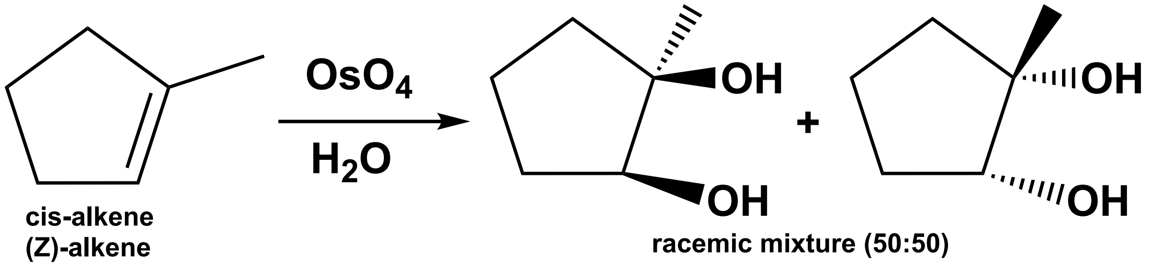
This molecule is a diterpene. It has 20 carbons, so 4 isoprene units (each composed of 5 carbons) and therefore two terpene units (10 carbons).
The numerous double bonds give this molecule a conjugated π system, all of these can undergo the dihydroxylation reaction.

Aside: Why not use OsO4 all the time?

Prices (per 1 kg)

Alkene/O_2	\$1-10
$KMnO_4$	\$100
OsO_4	\$100,000

Example 2



Note: the stereochemistry around the double bond in the starting material is important when determining the products of a reaction. *(stereospecific reaction)*

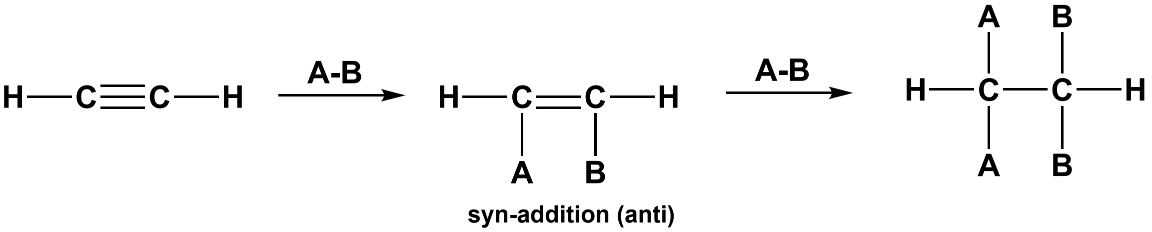
Recall the differences amongst carbons with single, double, and triple bonds:

Properties	alkane	alkene	alkyne
Hybridization	sp^3	sp^2	sp
C-C ΔH_d (kcal/mol)	90	173	229
Distance (C-C, Å)	1.54	1.33	1.20
Distance (C-H, Å)	1.1	1.07	1.0

→ alkynes are very reactive, highly energetic compounds

<u>Reactions of Alkynes</u>

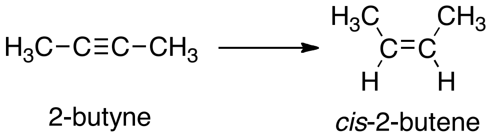
1. Addition (analogous to alkenes)



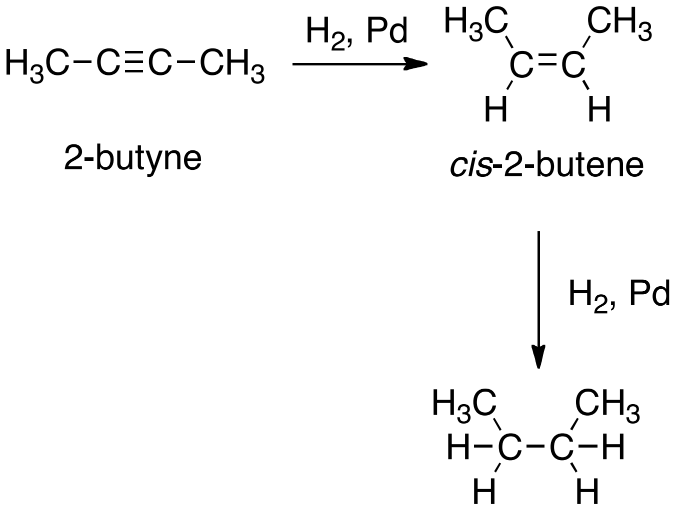
However, in a solution of 'AB' the reaction would not stop at the alkene. The AB species will add again (with A and B going to same carbon as before) to give an alkane product.

Addition reactions

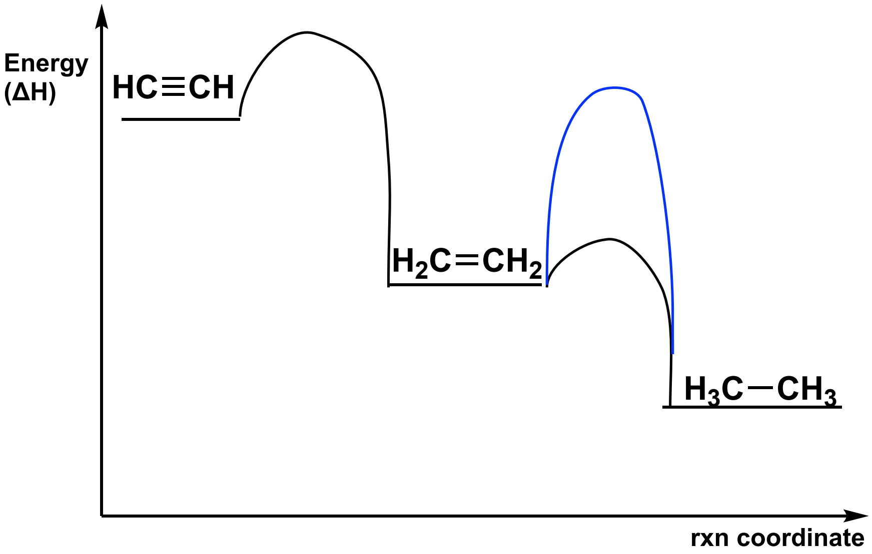
<u>1. Hydrogenation</u> *(syn addition)*



H_2 and catalyst (such as Pd or Pt)
However, a less reactive catalyst is needed to stop reaction at the cis-2-butene product. Otherwise, the reaction continues to the alkane as shown below.



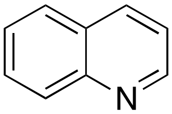
Energy Diagram



How do we stop the reaction at our desired alkene? *We raise the activation energy of the second reaction!*

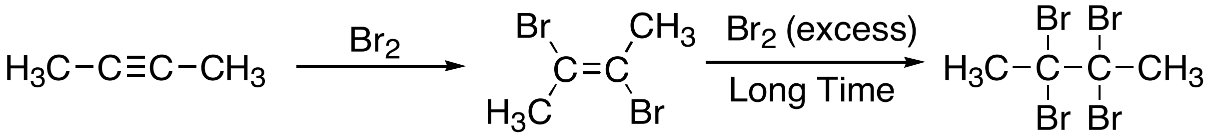
Lindlar's Catalyst:

Pd, $BaSO_4$ (or $CaCO_3$ is often used in place of $BaSO_4$), and quinoline (see below):

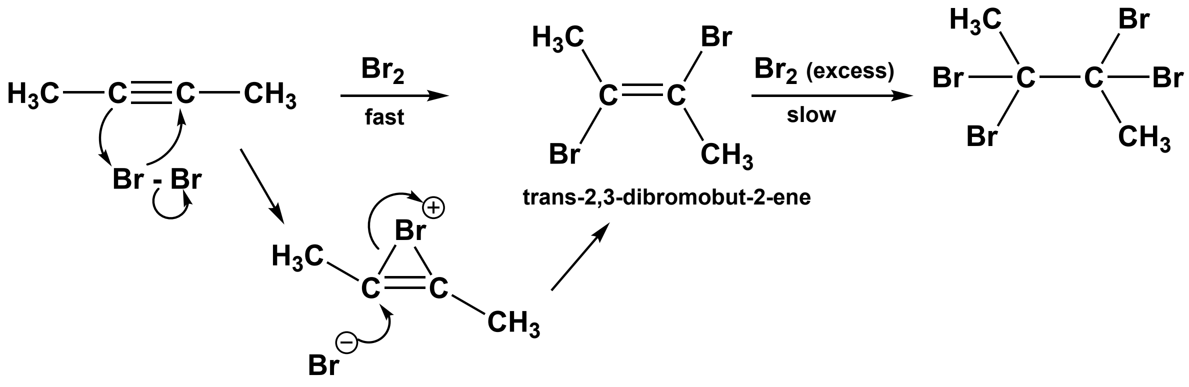


- These conditions allow for selective hydrogenation of alkynes to alkenes.

2. Halogenation *(trans or anti addition)*

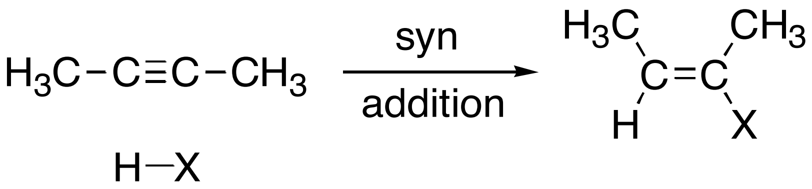


Mechanism



3. HX Addition *(mostly syn)*

X= Cl, Br, I



Example Addition of HCl to propyne (*follows Markovnikov's rule*)