Exam 2: REVISED

Rooms (11/05/09)

8 - 9:20 A.M.

① STO B50 A - L

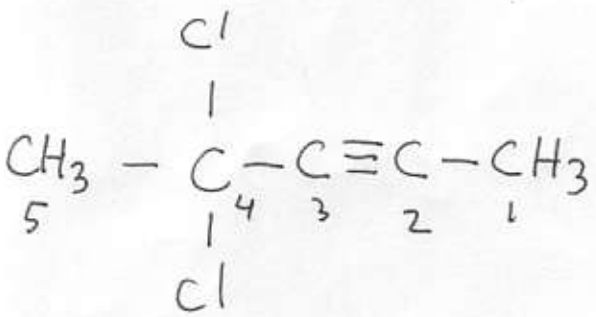
② CAS 211 M - R

③ SED 130 S - Z

School

Lecture 15 10/29/09

Alkynes and Naming



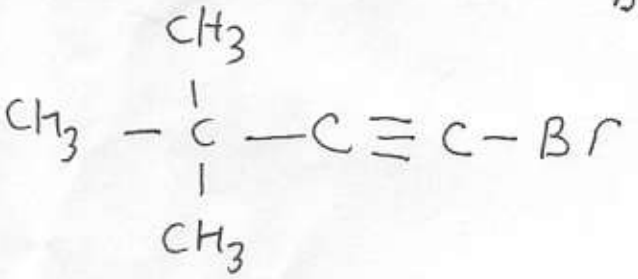
4,4-dichloro-2-pentyne

or

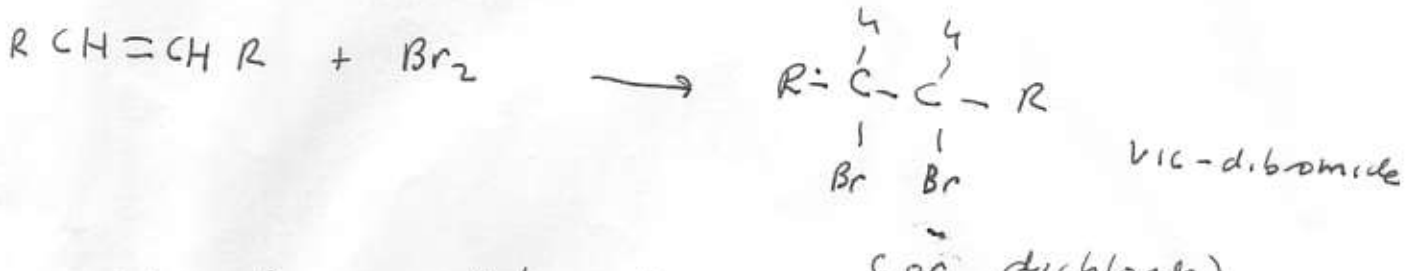
4,4-dichloro-pent-2-yne

1-bromo-3,3-dimethyl-1-butyne

but-1-yne

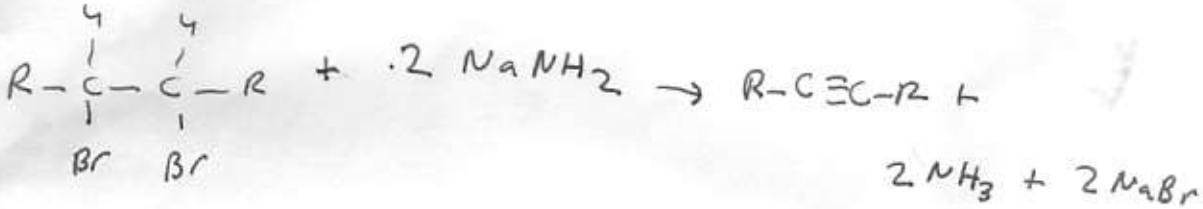


Synthesis of Alkynes by Elimination RXS:

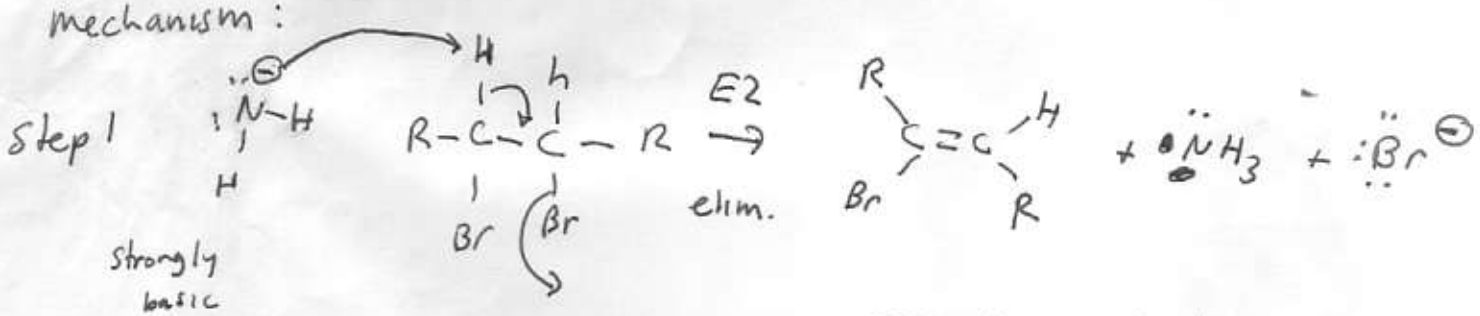


vic-dibromide is dehydrohalogenated through reaction with strong base

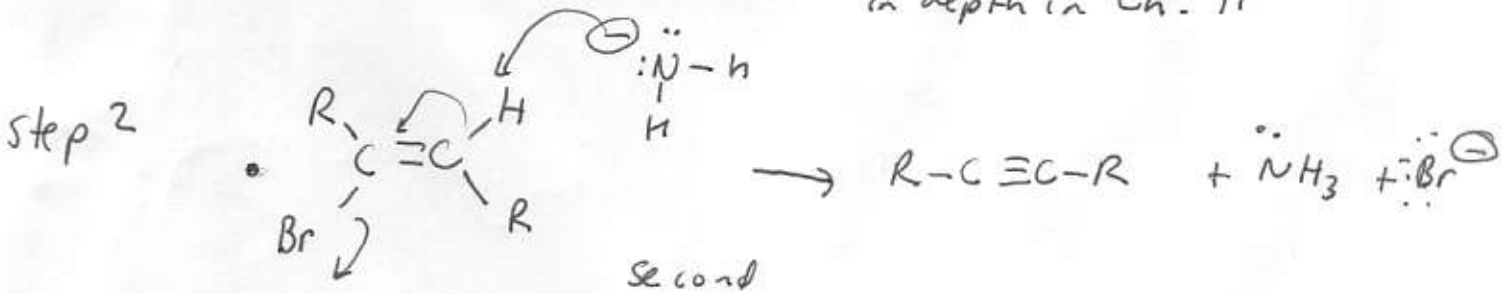
Reaction:



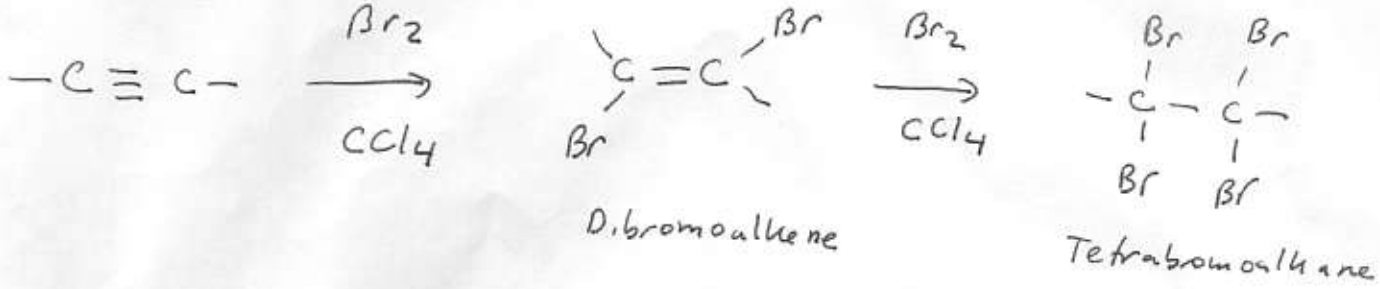
mechanism:



E2 elim. will be considered in depth in Ch. 11



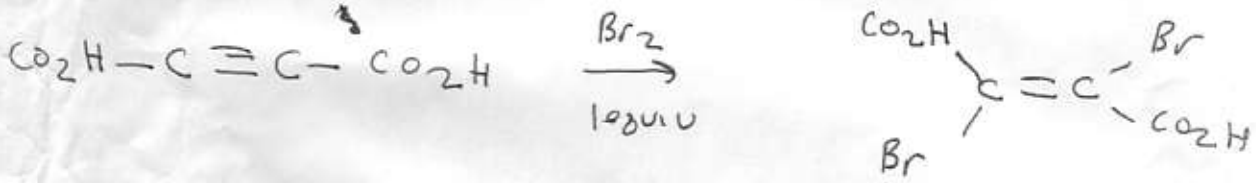
Addition of Bromine and Chlorine to Alkynes



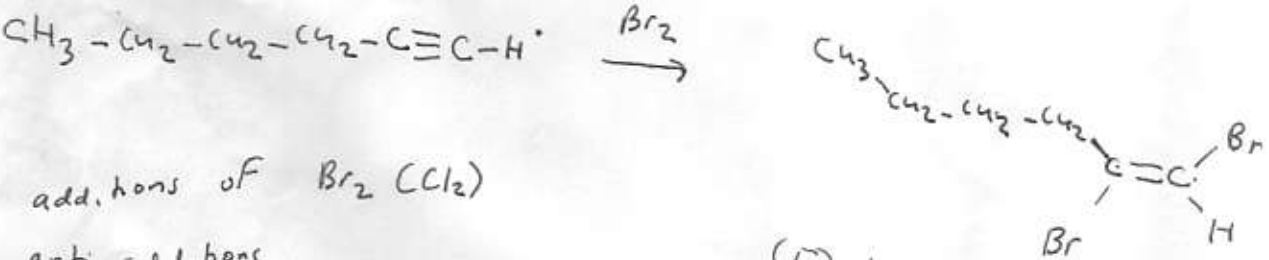
Dibromoalkene

Tetrabromoalkane

- Alkynes react with Br_2 in an addition reaction
- Addition may occur once or twice depending of # of equivalents of halogen employed

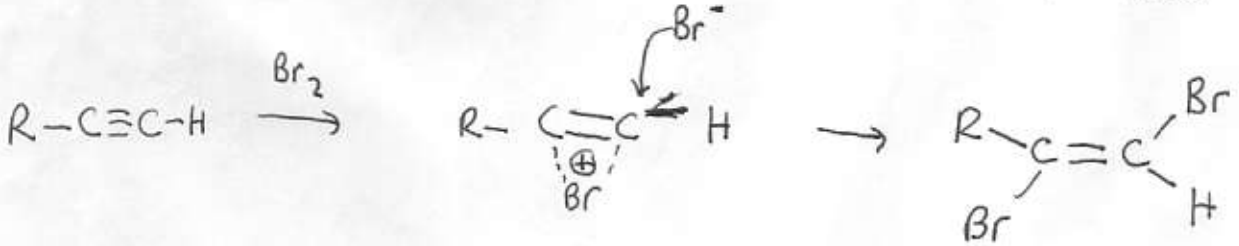
1) 

trans-dibromoalkene

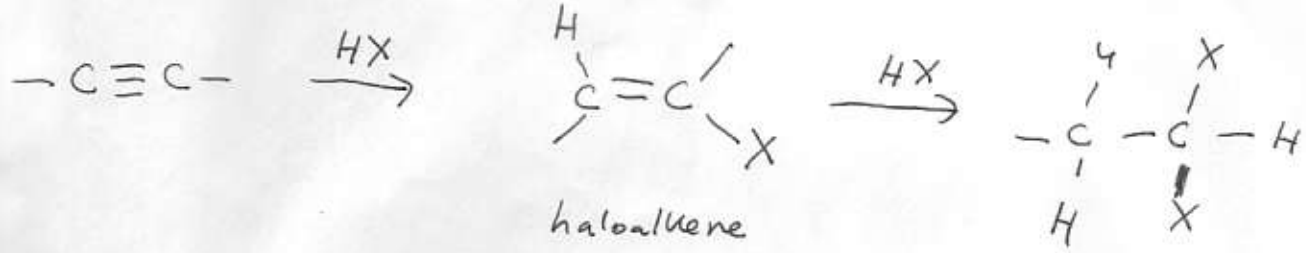
2) 

Most additions of Br_2 (Cl_2) are anti additions

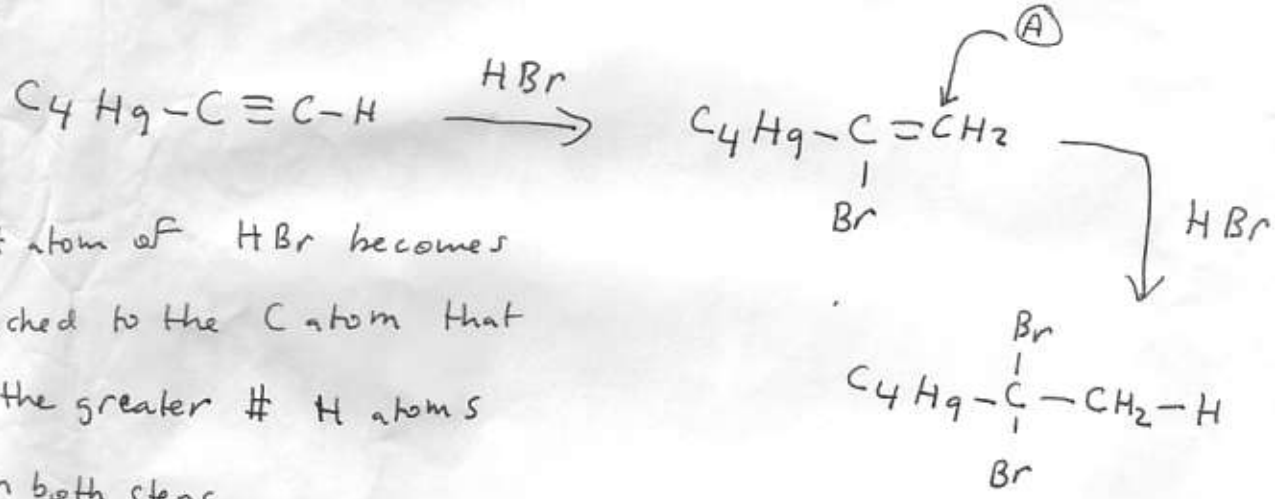
(E)-1,2 dibromohexene



Addition of Hydrogen Halides to Alkynes

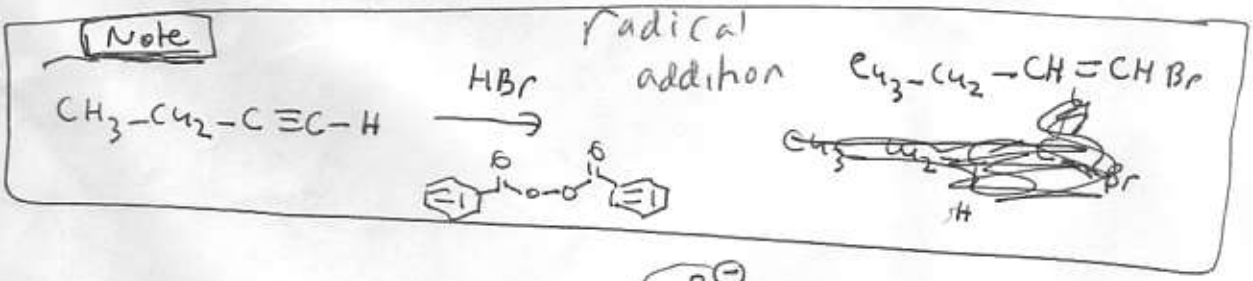


Both additions are regioselective & follow Markovnikov's rule:

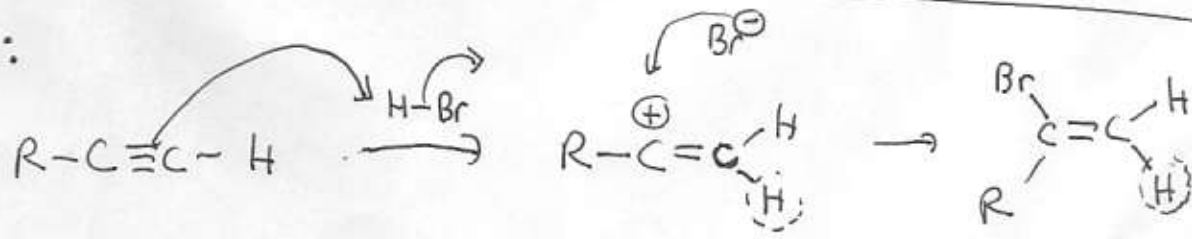


(A) H atom of HBr becomes attached to the C atom that has the greater # H atoms in both steps

Note



Mechanism:



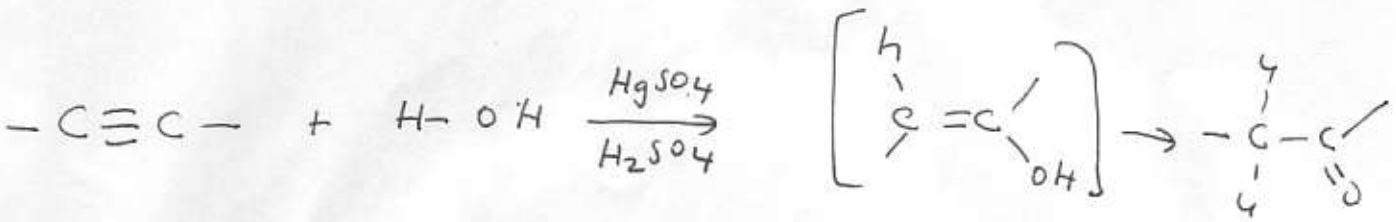
Vinylic carbocation

- has sp hybridized C
- generally forms less readily than alkyl carbocation

- general rule: about as stable as 1° alkyl carbocation

vinyl bromide

Hydration of Alkynes : Synthesis of Ketones

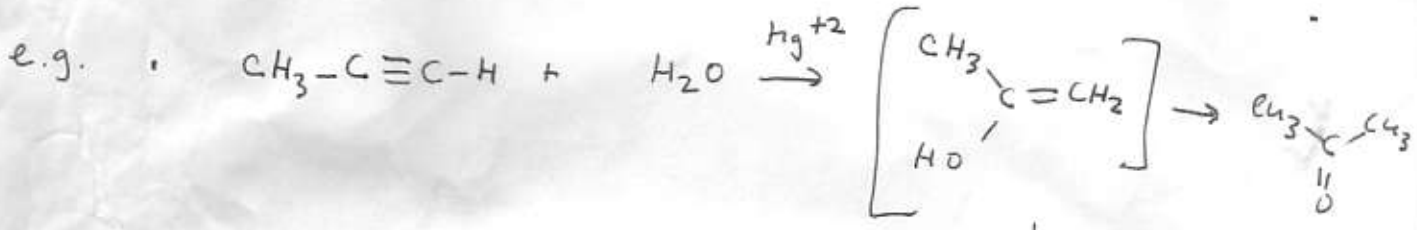


"enol" (vinylic alcohol)

ketone

-OH group adds to more highly subst carbon:

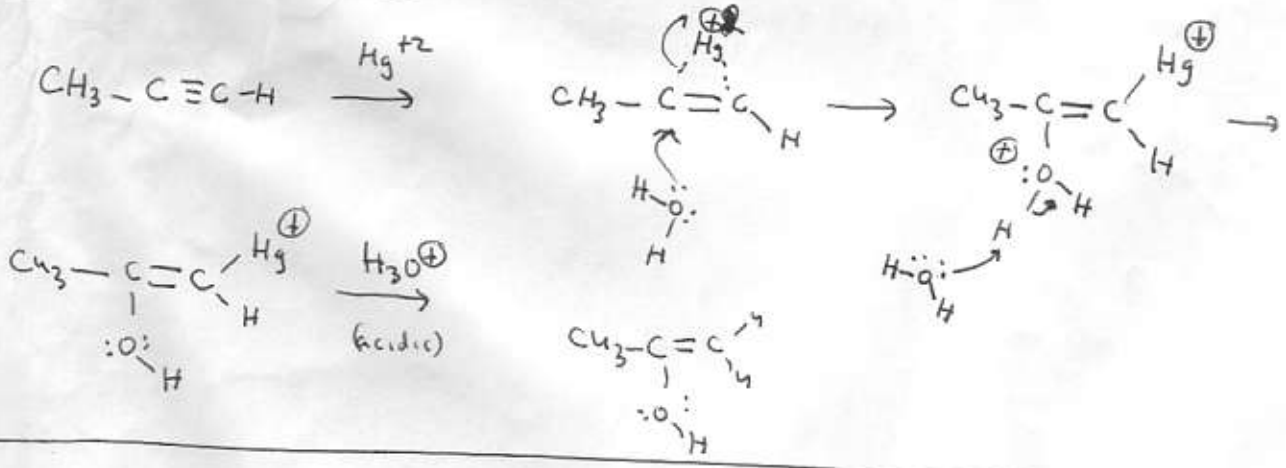
e.g. :



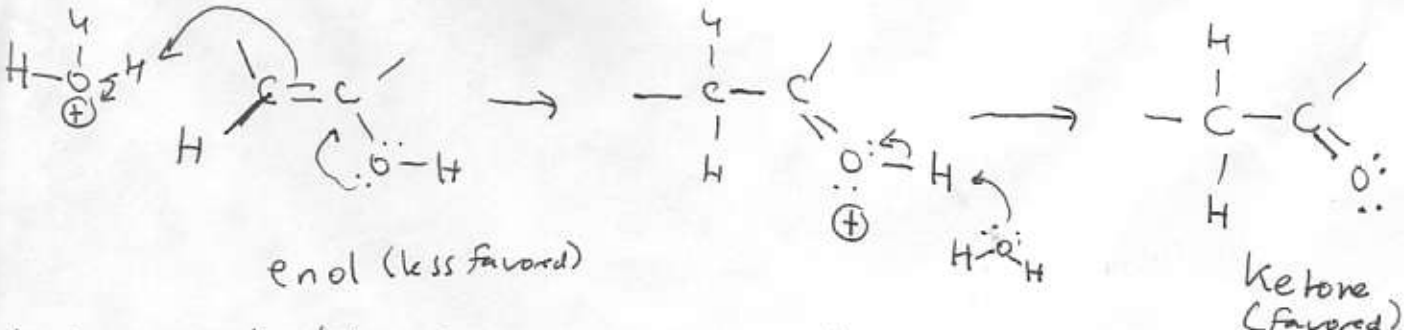
enol

Acetone

Mechanism for 1st step



Mechanism for enol → ketone:



enol (less favored)

ketone (favored)

Keto enol tautomerism process

tautomers: constitutional isomers that interconvert rapidly

Hydrogenation of Alkynes

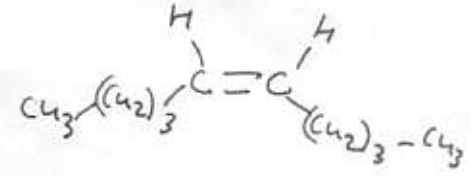
$CH_3-C\equiv C-CH_3 \xrightarrow[H_2\ 1\text{ equiv}]{Pt\text{ or }Pd} [CH_3-CH=CH-CH_3] \xrightarrow[H_2\ \text{second equiv.}]{Pt\text{ or }Pd} CH_3-CH_2-CH_2-CH_3$

- Pd/C typically leads to complete reduction to the alkane
- Lindlar catalyst ($Pd/CaCO_3$ with quinoline) used to stop hydrogenation of the alkene

$CH_3(CH_2)_3-C\equiv C-(CH_2)_3CH_3 \xrightarrow[2\ H_2]{Pd/C} CH_3(CH_2)_8CH_3$

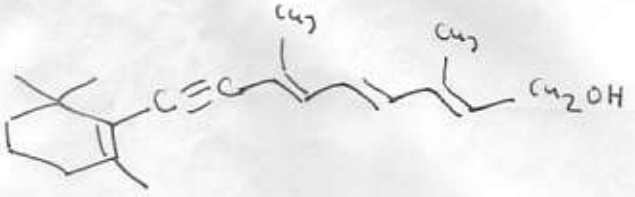
5-decyne → decane

$\xrightarrow[Lindlar]{H_2}$

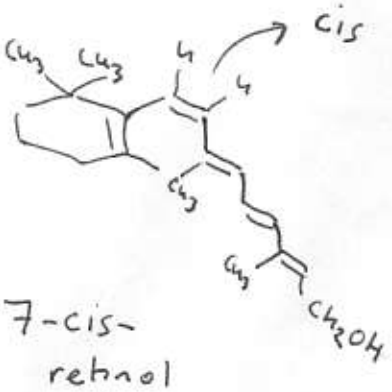


cis-5-decene

Hydrogenation with Lindlar's catalyst occurs with syn addition of H's



$\xrightarrow[Lindlar]{H_2}$



7-cis-retinol

(Hoffmann LaRoche)

Vitamin A intermediate