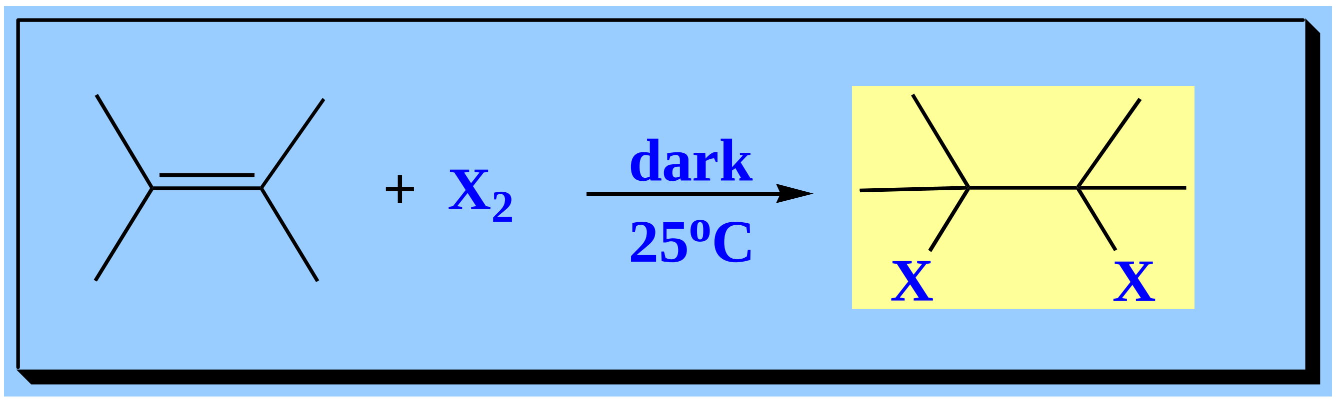
Section 12--Electrophilic Addition of Bromine and Chlorine to Alkenes

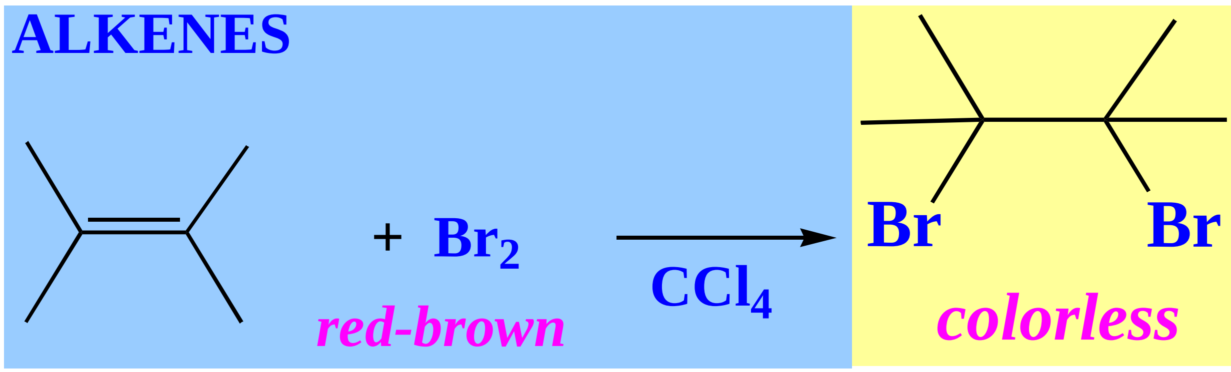
Addition of Bromine and Chlorine to Alkenes

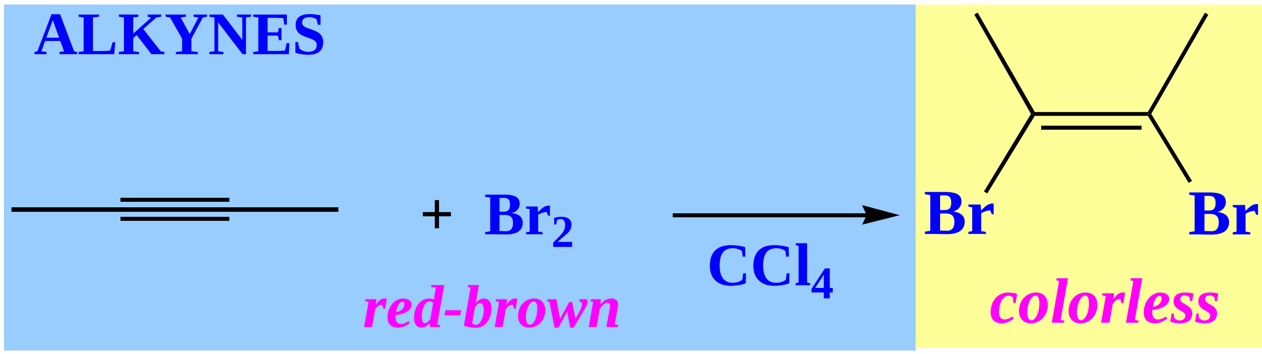
Alkanes do not react with Br_2 or Cl_2 in the absence of ultraviolet or visible light at room temperature.

Alkenes rapidly undergo additions reactions with Br_2 and Cl_2 in the dark (no radiation) at room temperature:



The Bromination Reaction as a Diagnostic Test for Alkenes and Alkynes





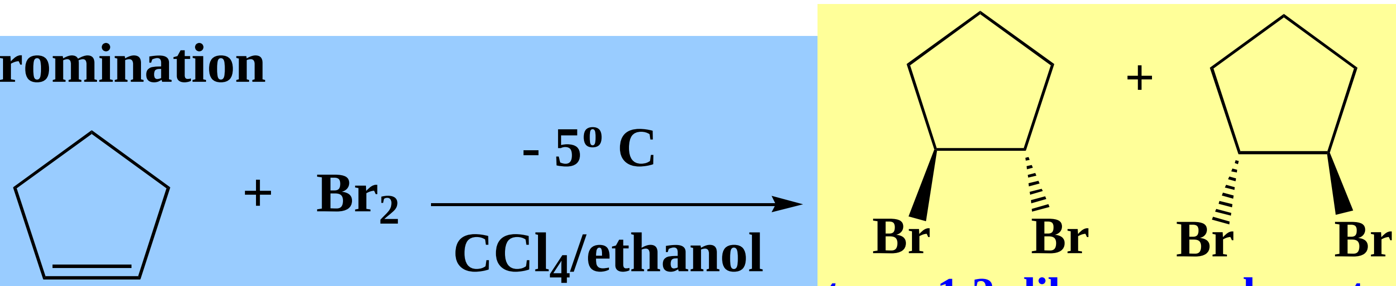
Examples of the Halogenation Reaction

Chlorination

$$CH_3CH_2CH{=}CH_2 + Cl_2 \xrightarrow{-9^o\ C} CH_3CH_2CHClCH_2Cl$$

1-butene → **1,2-dichlorobutane**

Bromination



cyclopentene → ***trans*-1,2-dibromocyclopentane**

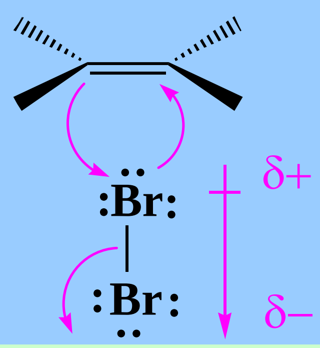
(Racemic Form)

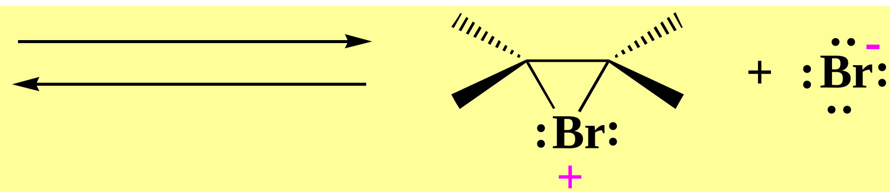
Note: Only the *trans*-1,2-dibromocyclopentane is formed. This result is understandable when the mechanism of this reaction is examined.

A Mechanism for the Bromination Reaction

The proposed mechanism for bromination of an alkene follows the general two-step mechanism of addition. The first step is electrophilic attack by the Br_2 on the p bond to give a cation intermediate, a bridging bromonium ion that controls the stereochemistry of the addition reaction.

Step 1 Electrophilic Attack



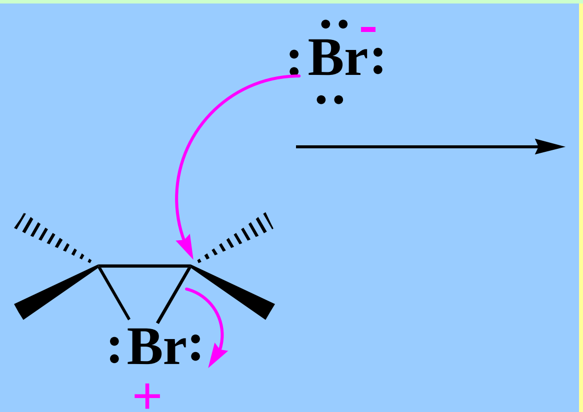


bromonium ion

As the Br_2 approaches the alkene, the exposed π electrons induce a polarization of the nonbonding electrons in the Br_2.

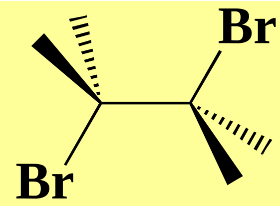
The closer electropositive bromine atom attaches to the two carbons of the alkene simultaneously to form a bridging bromonium ion.

Step 2 Nucleophilic Addition

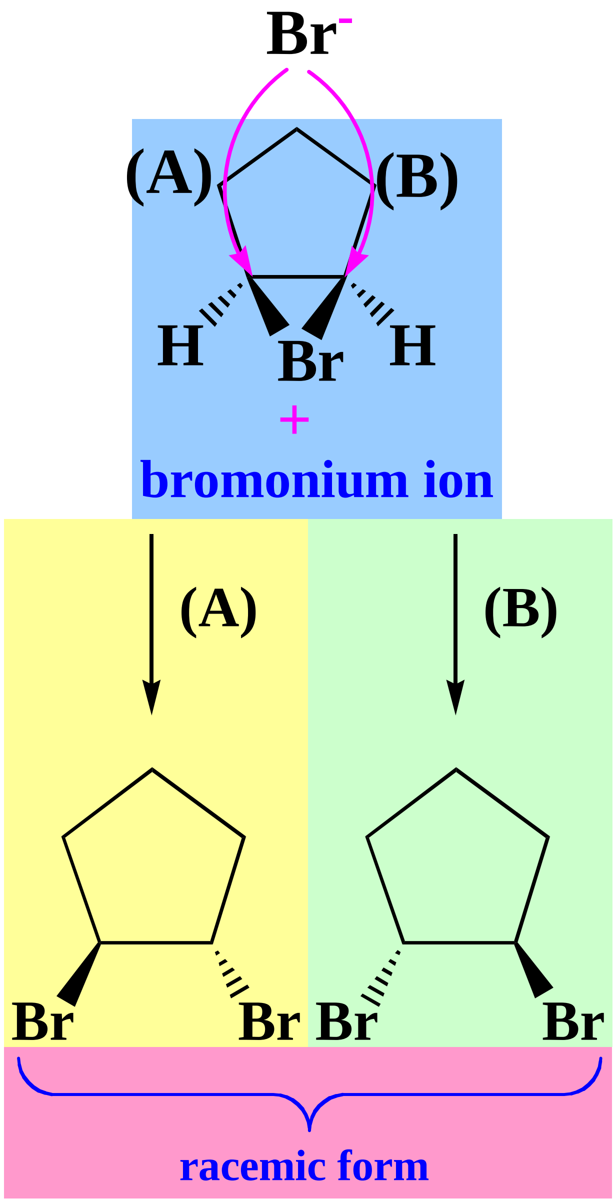


bromonium ion

The nucleophilic bromide ion attacks the carbon in an S_N2 reaction and opens the ring of the bromonium ion.



The vicinal dibromide is formed with a well-defined stereochemistry in an overall anti-addition.



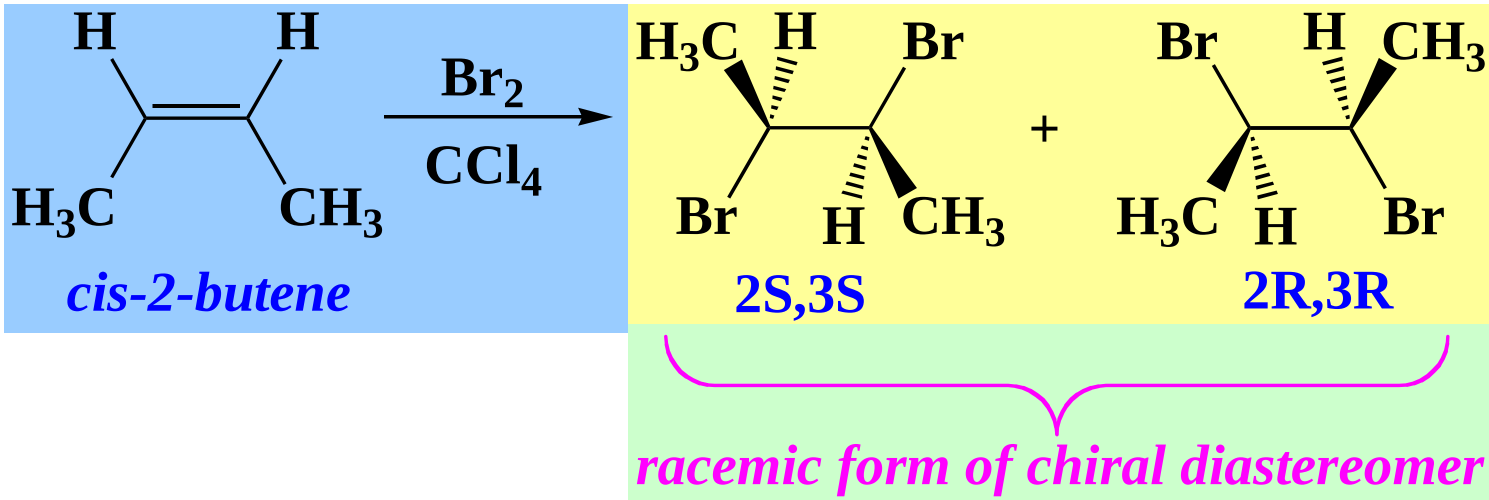
Nucleophilic attack by bromide ion in an S_N2 reaction yields the *trans* -1,2-dibromide.

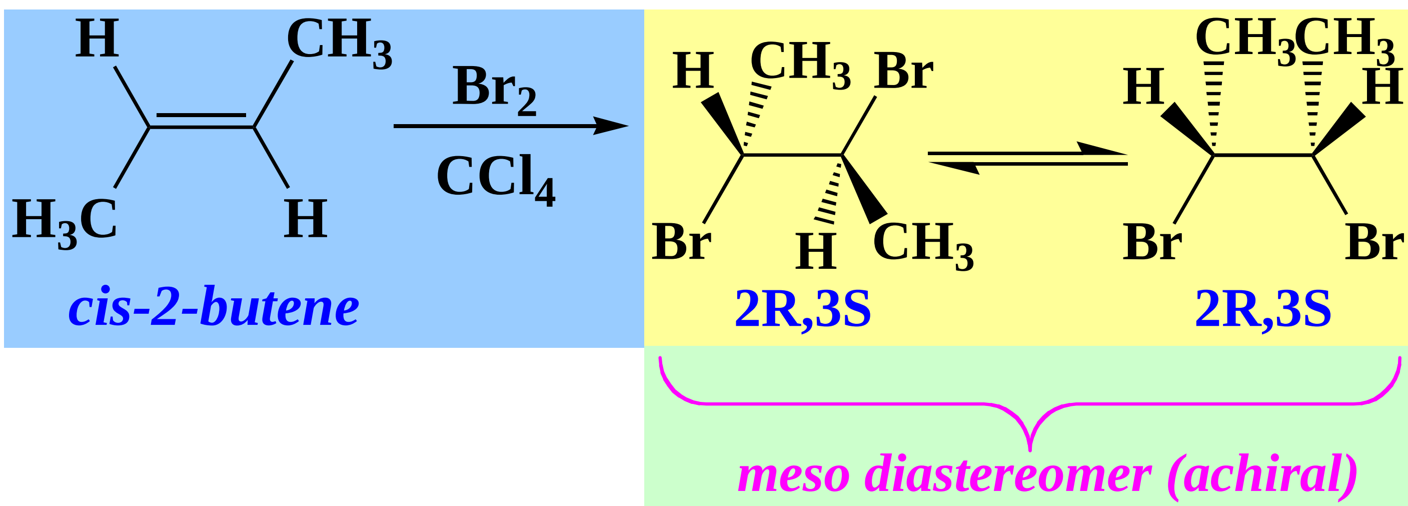
Because of the structural symmetry of the cyclopentyl bromonium ion, reaction by paths (A) and (B) occur with equal probability .

Stereospecific Reactions

A reaction where one particular stereoisomeric form of the starting material reacts to give a particular stereoisomeric form of the product is a stereospecific reaction. In such reactions, the reaction mechanism introduces stereospecificity. The brominations of cyclopentene and cyclohexene are examples of stereospecific reactions.

The brominations of *cis*- and *trans*-2-butene are stereospecific reactions.

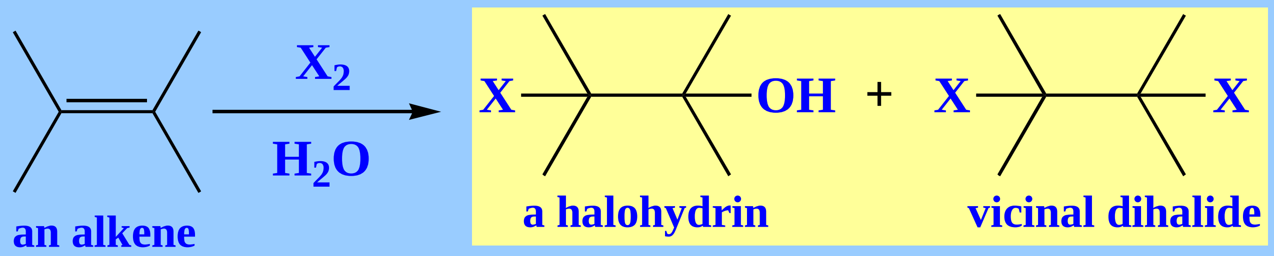




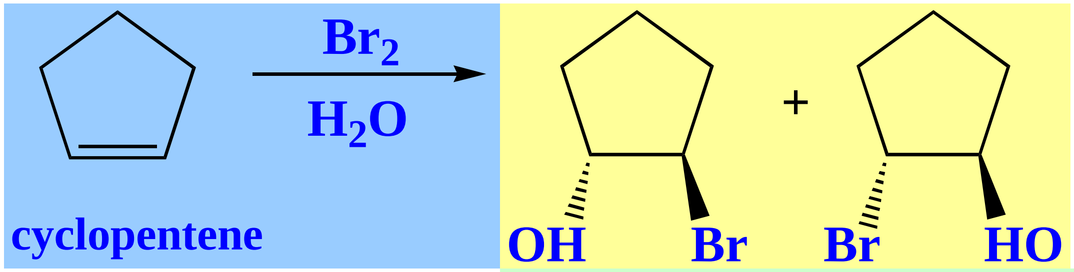
Halohydrin Formation

When the halogenation reaction is carried out in the presence of other nucleophiles that compete with halide ion, other addition products are formed.

In water, H_2O is a competing nucleophile:



Example: Reaction of Cyclopentene

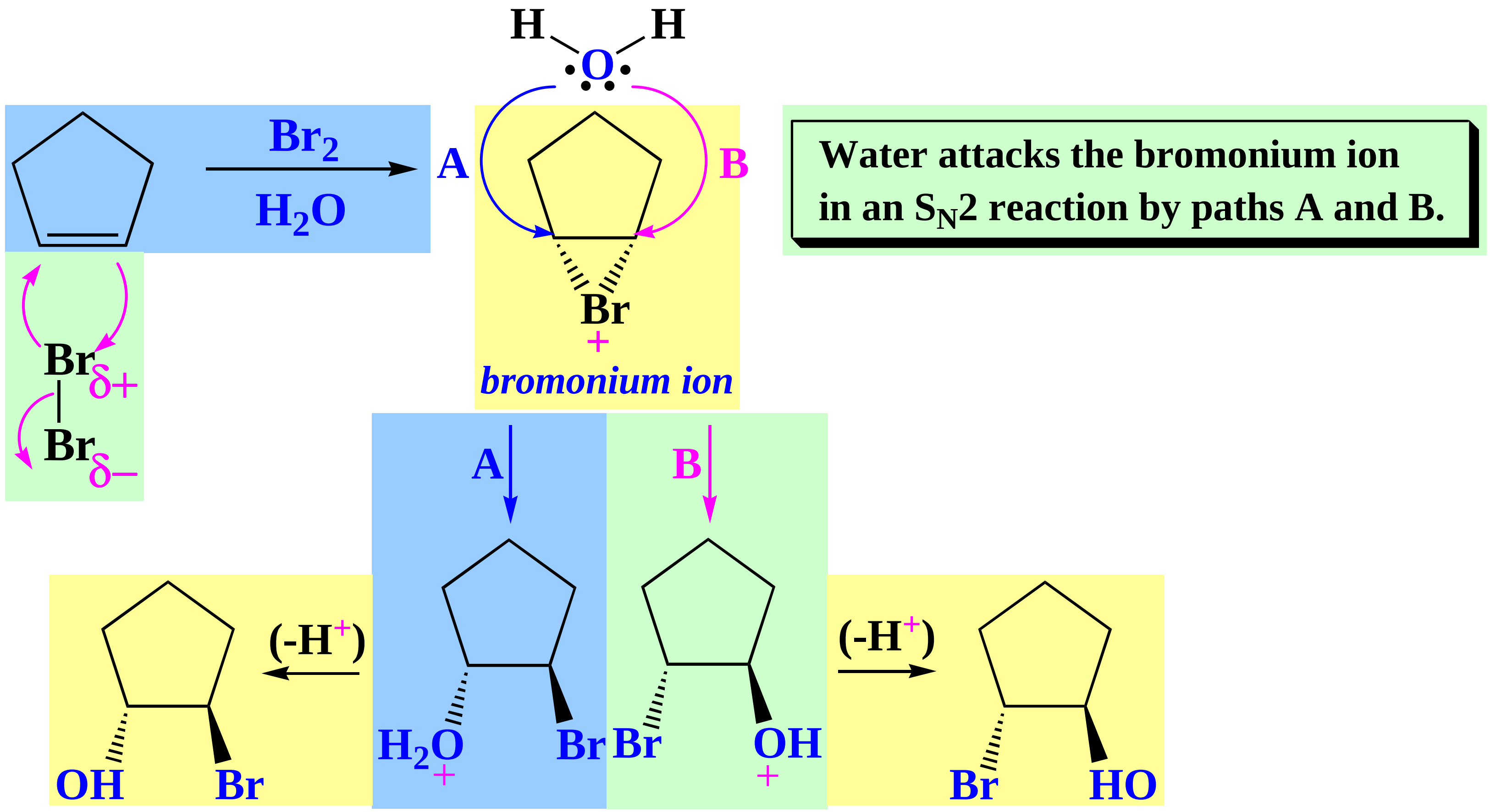


***trans*-2-bromocyclopentanol**

(as a racemic form)

A Mechanism for Bromohydrin Formation

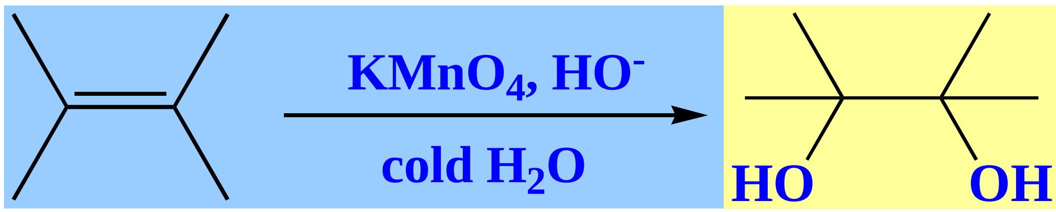
Bromohydrin formation is a stereospecific reaction. This reaction specificity is explained by the formation and reaction of a bromonium ion intermediate.

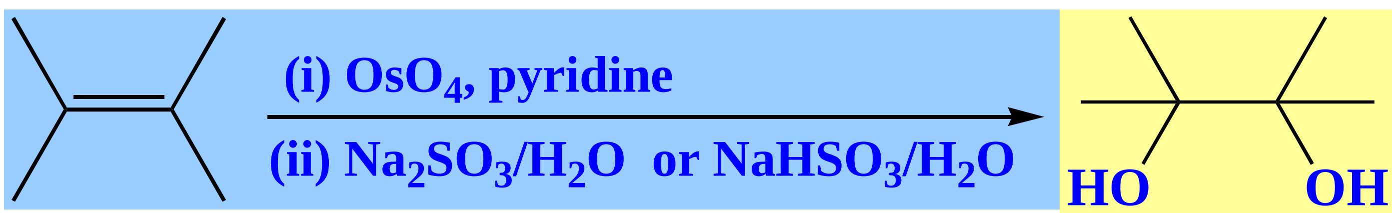


Section 16--Oxidation of Alkenes: Syn 1,2-Dihydroxylation

Oxidations of Alkenes--Syn Hydroxylation

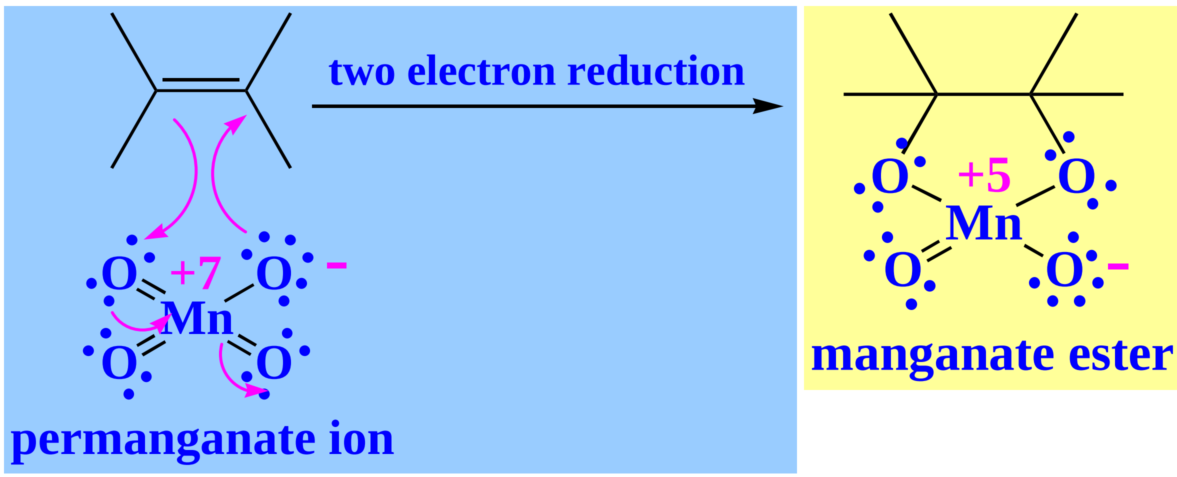
The stereospecific formation of 1,2-diols (or glycols) from alkenes may be carried out in two ways:

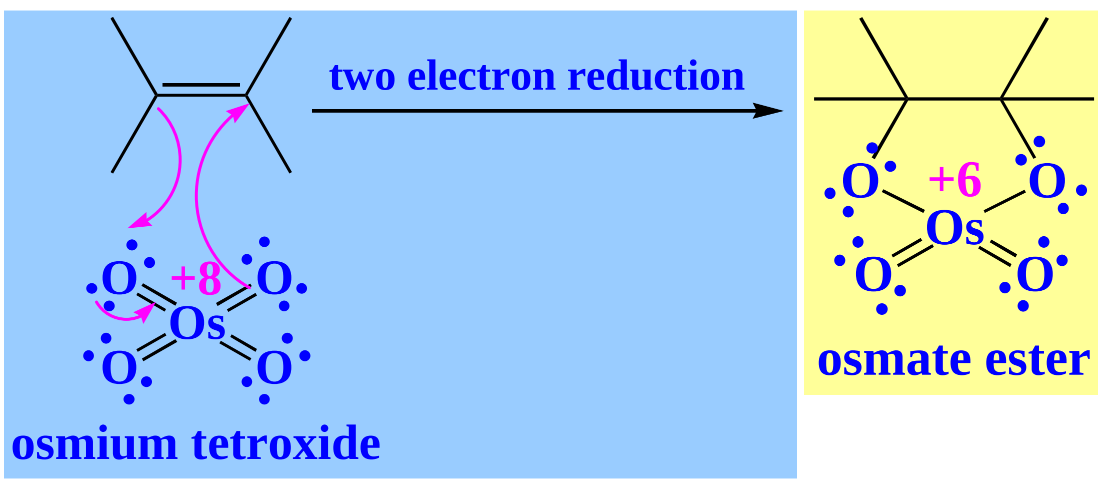




The Mechanism of the Hydroxylation Reaction

The mechanisms of the two hydroxylation reactions are very similar. The initial step is oxidative addition to the alkene to produce cyclic ester-type intermediates.

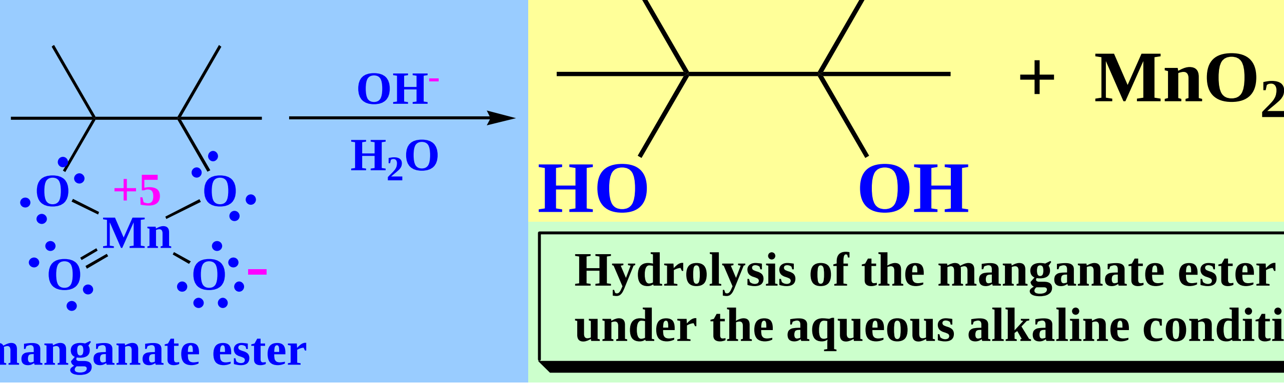




Conversion to 1,2-Diols

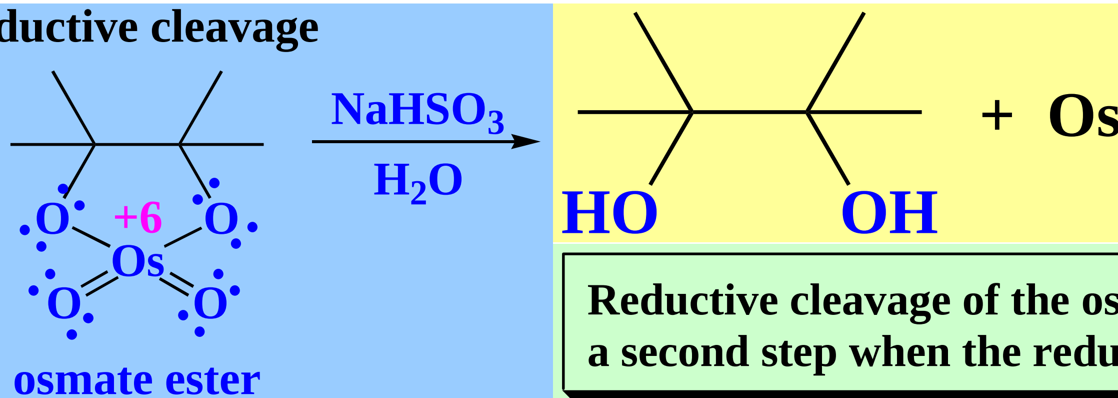
The syn stereochemistry of the hydroxylation reactions is set with formation of the cyclic intermediates. The cyclic esters are converted to the diols as follows:

alkaline hydrolysis



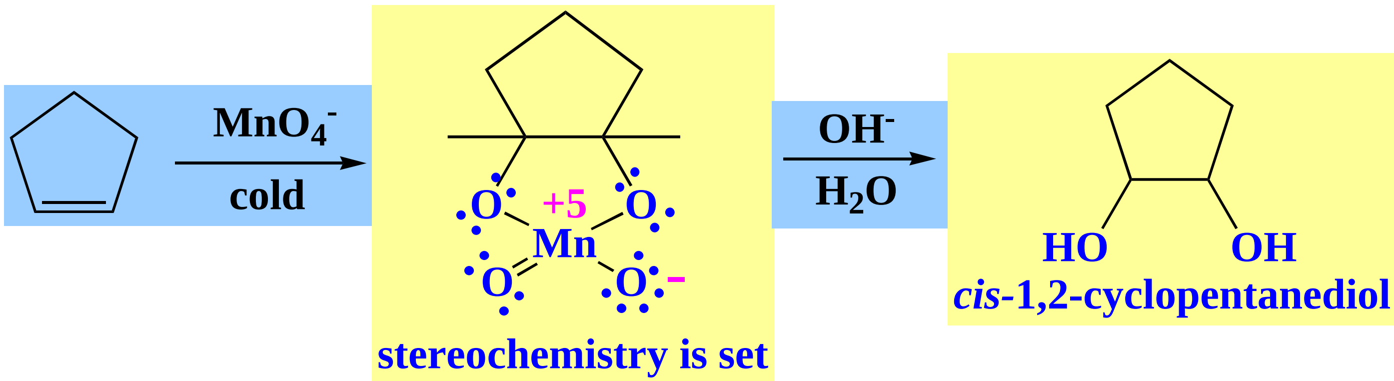
Hydrolysis of the manganate ester occurs under the aqueous alkaline conditions.

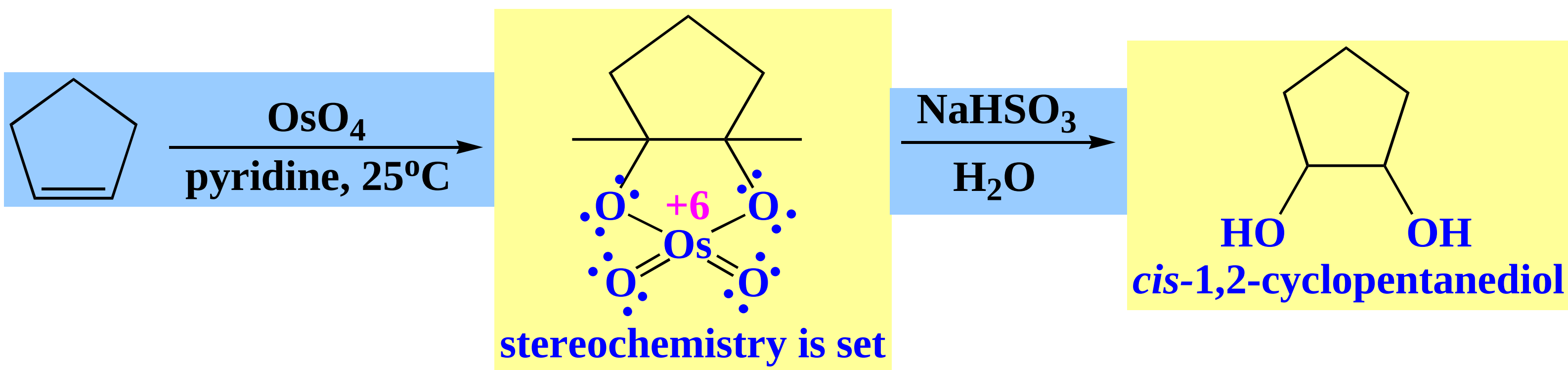
reductive cleavage



Reductive cleavage of the osmate ester occurs in a second step when the reducing agent is added.

Examples of Syn-Hydroxylation





Section 17--Oxidative Cleavage of Alkenes

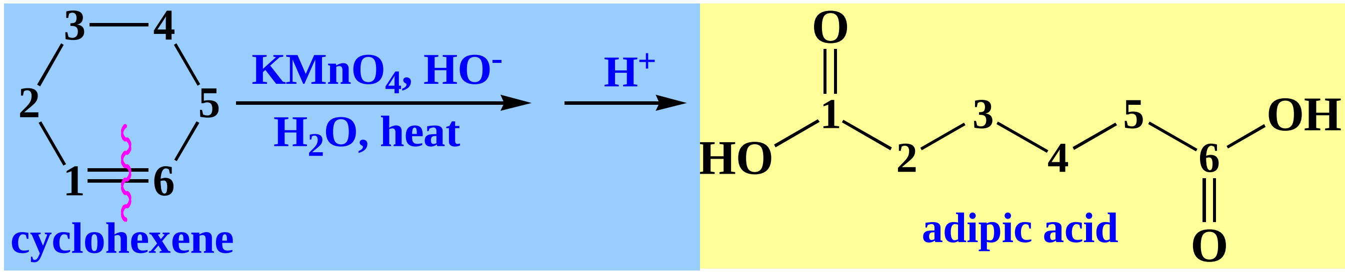
Oxidative Cleavage Reactions of Alkenes

The oxidation of alkenes may be carried out with a variety of reagents for synthetic and diagnostic purposes.

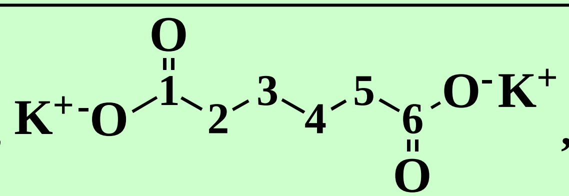
Oxidative-Cleavage with Hot Potassium Permanganate

In these reactions with the strong oxidant, $KMnO_4$, a 1,2-diol (glycol) is probably formed first with subsequent further oxidation and C-C bond cleavage.

Examples of Oxidative-Cleavage with Hot Potassium Permanganate

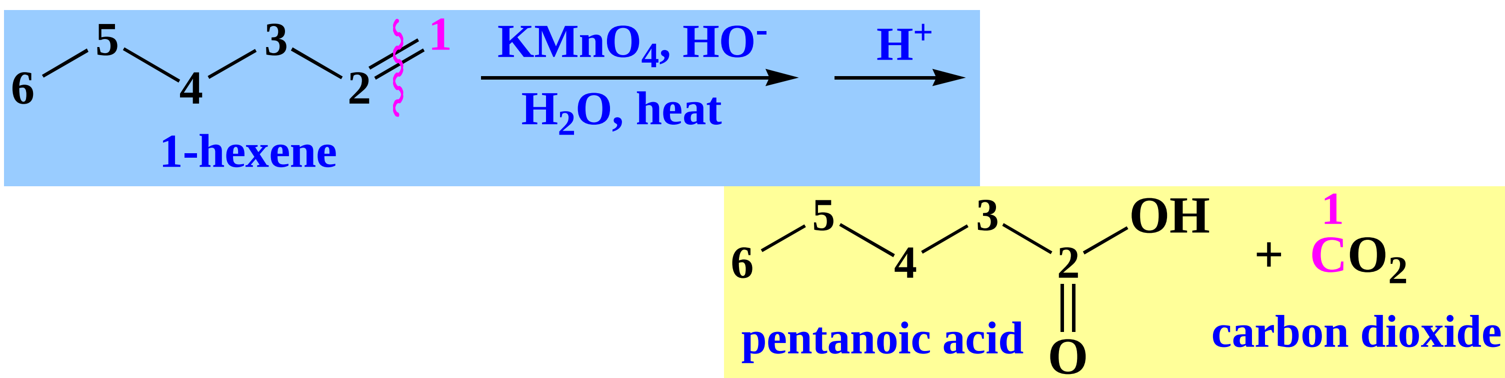


The dicarboxylate salt ,



, is produced initially which is neutralized by acid in a workup step.

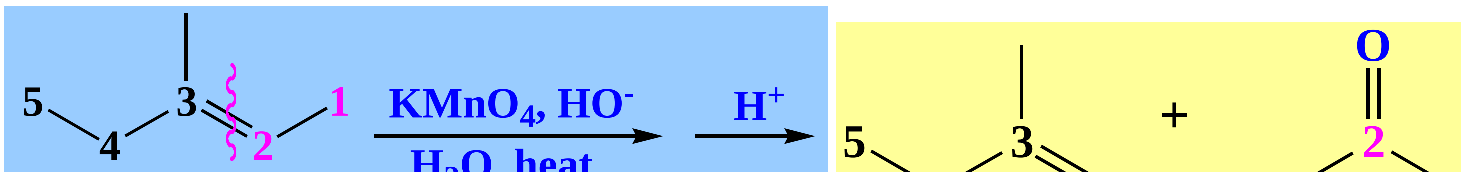
Terminal alkenes yield a carboxylic acid and CO_2:



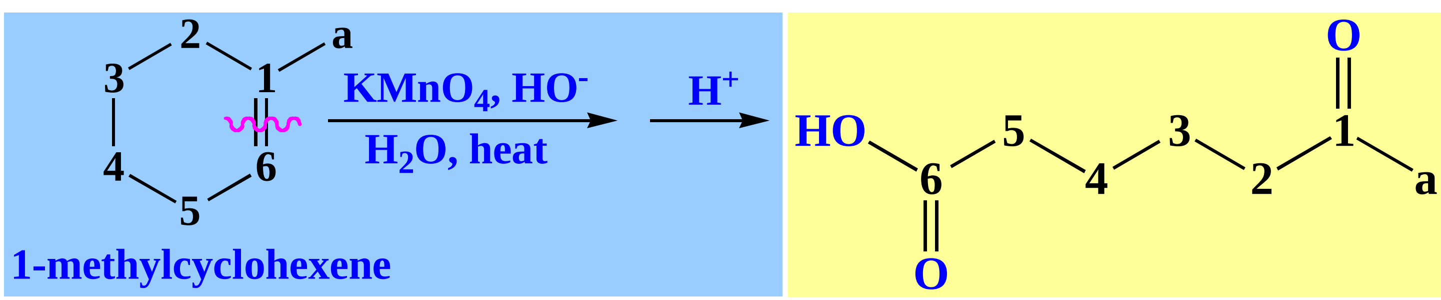
Predicting the Products of the Oxidative-Cleavage Reaction

In these oxidations, the carbons of the alkene are oxidized to the highest level possible. Products may be predicted by replacing the C=C with C=O + O=C and allowing for the further oxidation of aldehyde products to carboxylic acids.

Examples

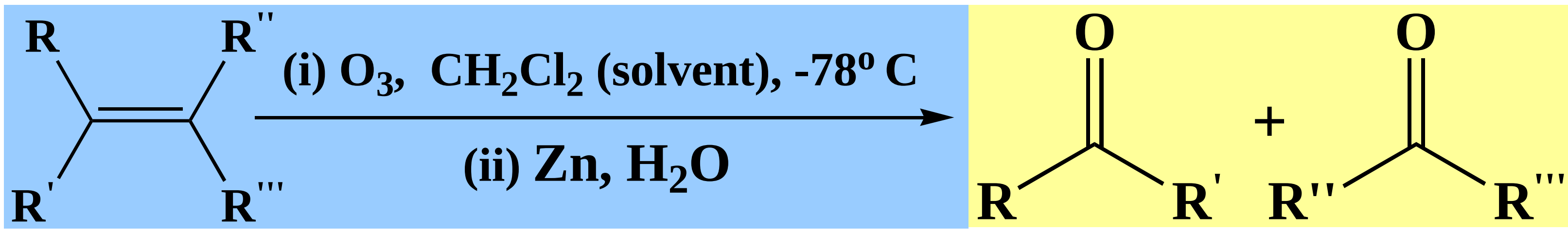


3-methyl-2-pentene



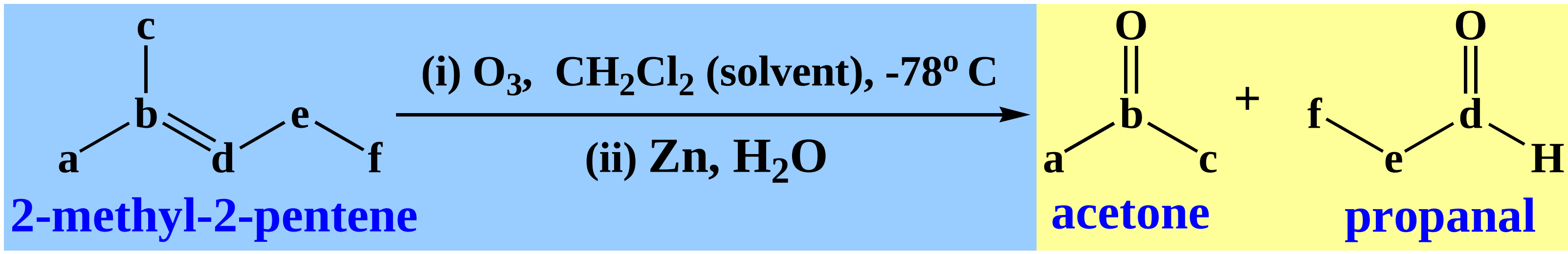
1-methylcyclohexene

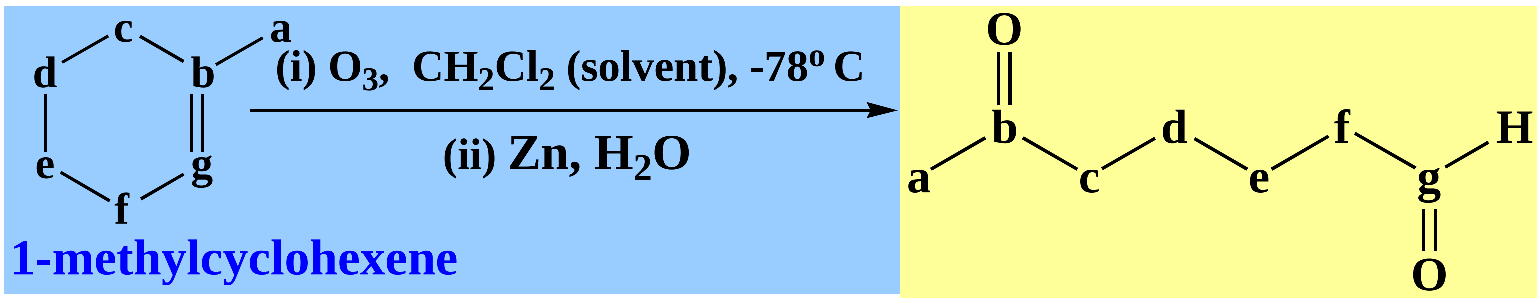
Overall reaction:



Note: Unlike oxidative cleavage with $KMnO_4$, aldehyde products are isolated because of the reductive workup conditions.

Examples of the Ozonolysis Reaction





Note: The products of ozonolysis will provide structural information about the alkene.

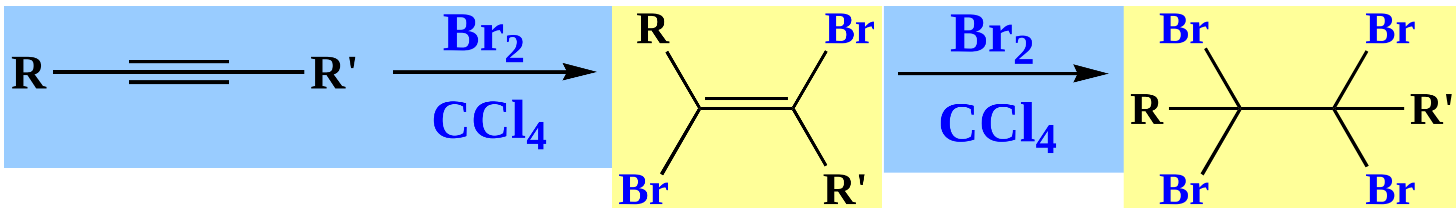
Section 18--Electrophilic Addition of Bromine and Chlorine to Alkynes

Section 19--Addition of Hydrogen Halides to Alkynes

Addition Reactions of Alkynes

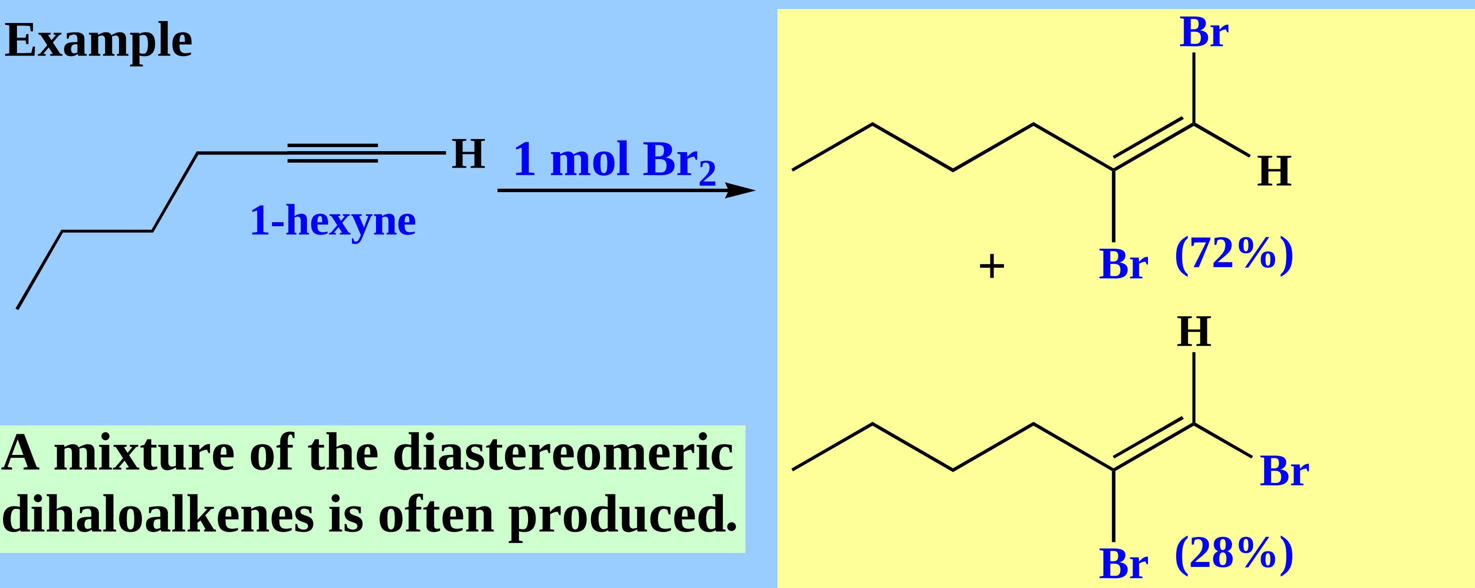
Alkynes undergo many of the same addition reactions as alkenes. Since the initial products are alkenes, they may react further.

Addition of Bromine or Chlorine



With care, the dihaloalkene products can be isolated:

Example



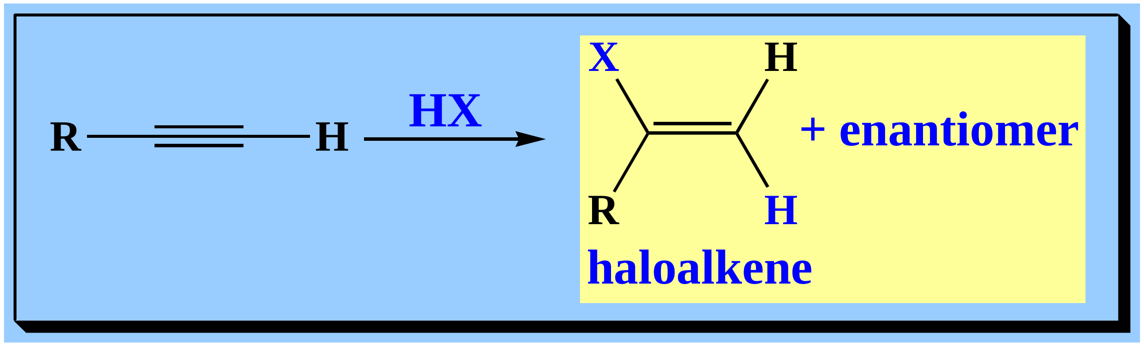
trans- and *cis*-1,2-dibromo-1-hexene

A mixture of the diastereomeric dihaloalkenes is often produced.

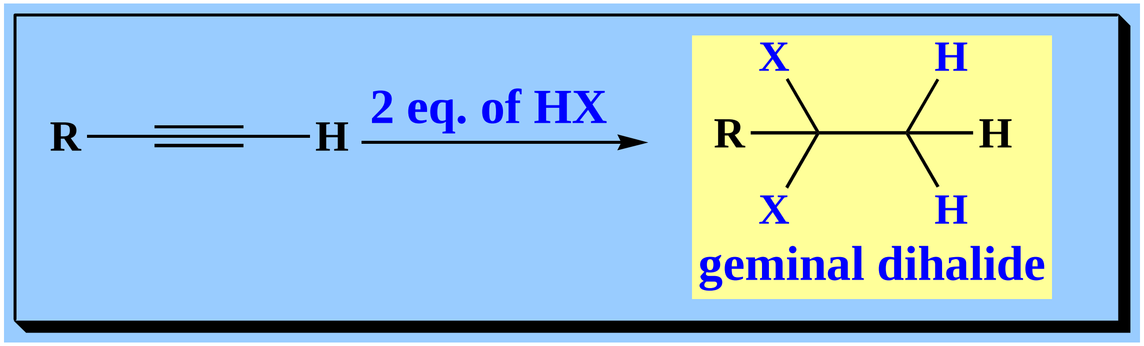
Addition of Hydrogen Halides to Alkynes

The addition of hydrogen chloride and hydrogen bromide to alkynes is regioselective (Markovnikov's rule) and may involve one or two equivalents of HX.

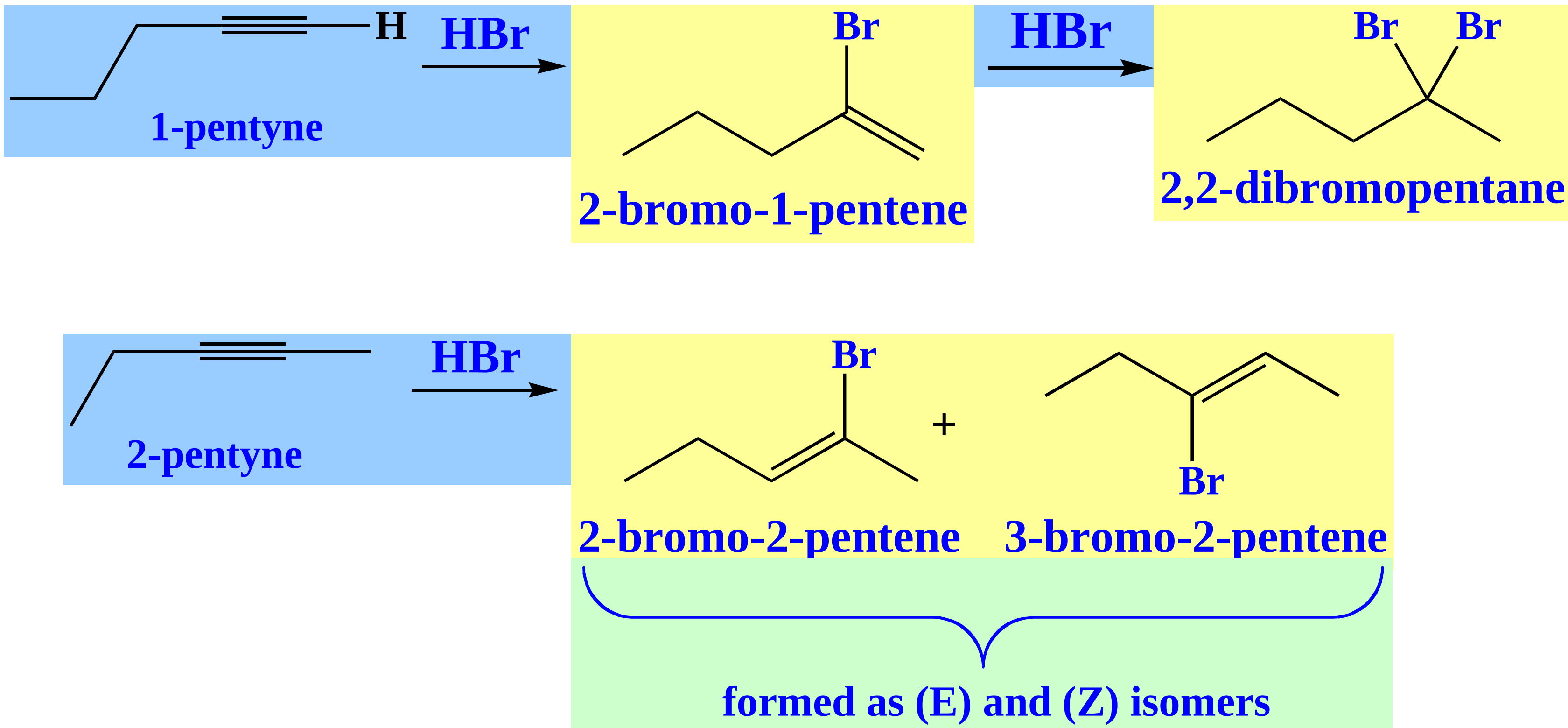
Addition of 1 equivalent of HX:



Addition of 2 equivalent of HX:



Some Examples

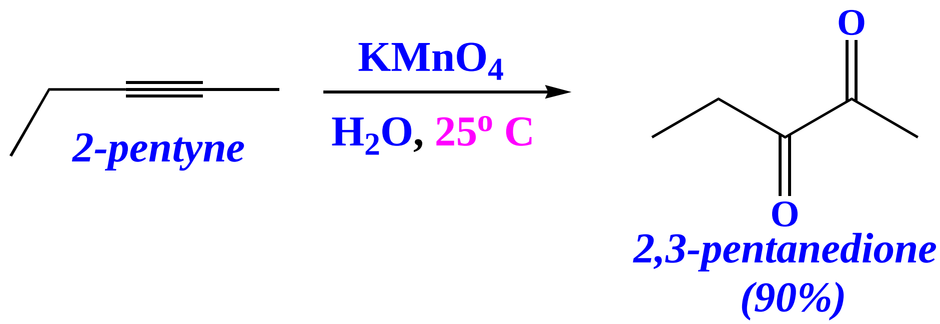


With 2-pentyne, there is no regioselectivity because of the similar stability of the two vinyl cation intermediates.

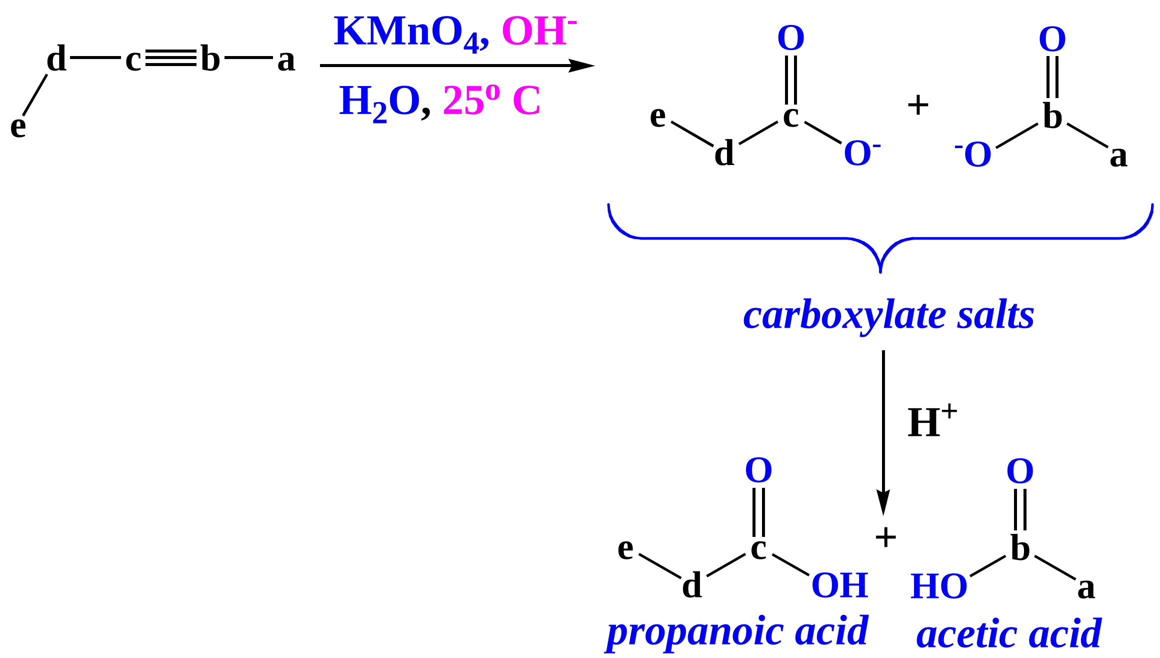
Section 20--Oxidative Cleavage of Alkynes

Oxidation by Potassium Permanganate

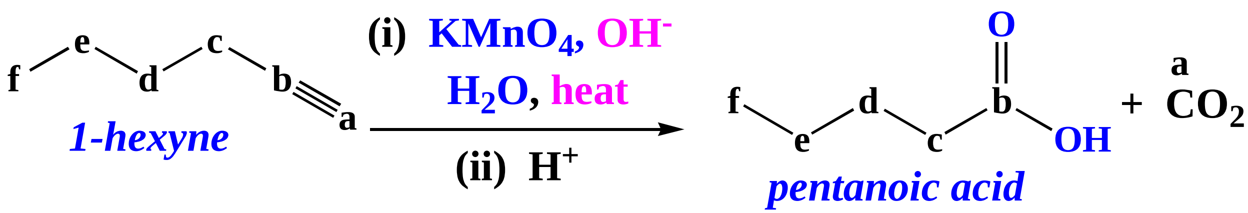
Mild conditions produce 1,2-diones:



Vigorous conditions result in oxidative-cleavage:



Vigorous Oxidation of Terminal Alkynes



Ozonolysis of Alkynes

Ozonolysis gives results similar to vigorous oxidation by $KMnO_4$: