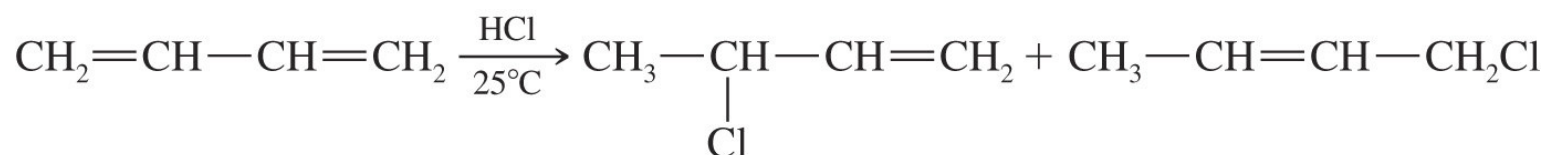




3.15 Additions to Conjugated Dienes

3.15.a Electrophilic Additions to Conjugated Dienes

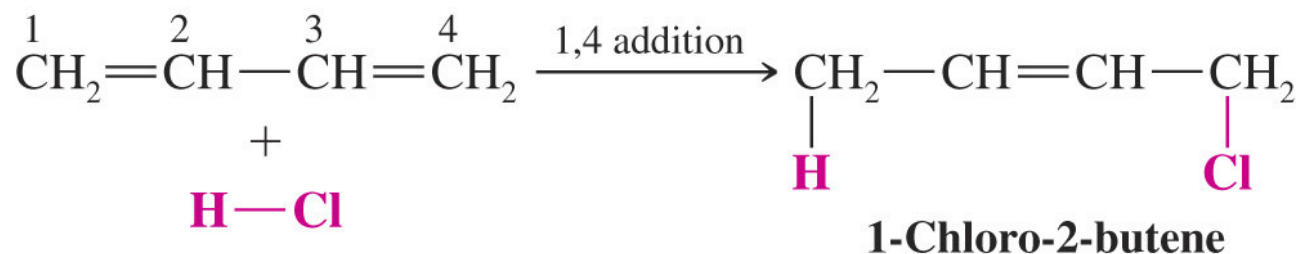
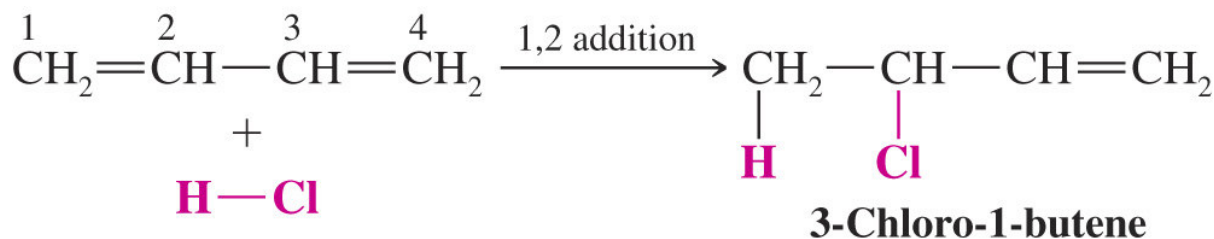
- Electrophilic Attack on Conjugated Dienes: 1,4 Addition
 - When 1,3-butadiene reacts with one equivalent of HCl at room temperature 78% of the **1,2 addition product** and 22% of the **1,4 addition product** are obtained



1,3-Butadiene

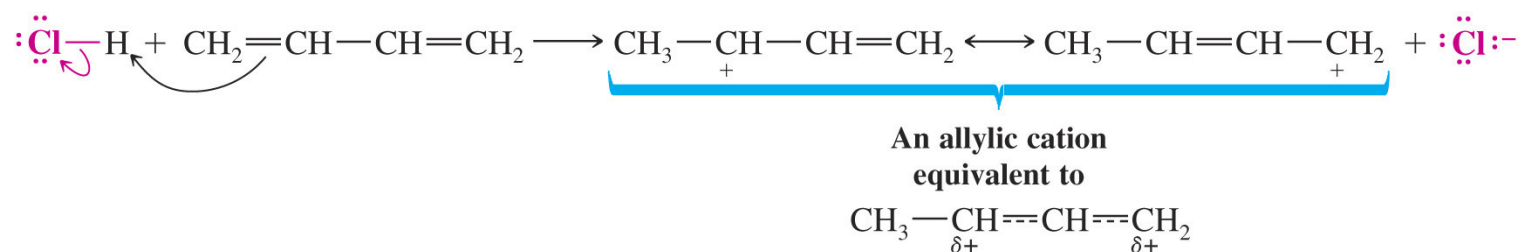
3-Chloro-1-butene
(78%)

1-Chloro-2-butene
(22%)

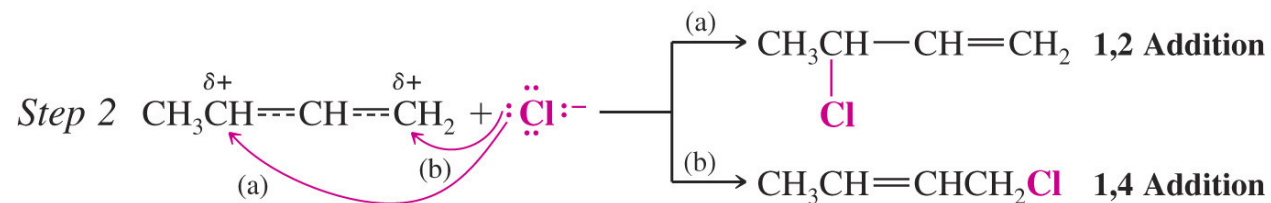


- In step 1 hydrogen chloride reacts to add hydrogen to a terminal carbon which gives a stable allyl cation intermediate
 - Addition of hydrogen to an internal carbon leads to an unstable 1° carbocation

Step 1

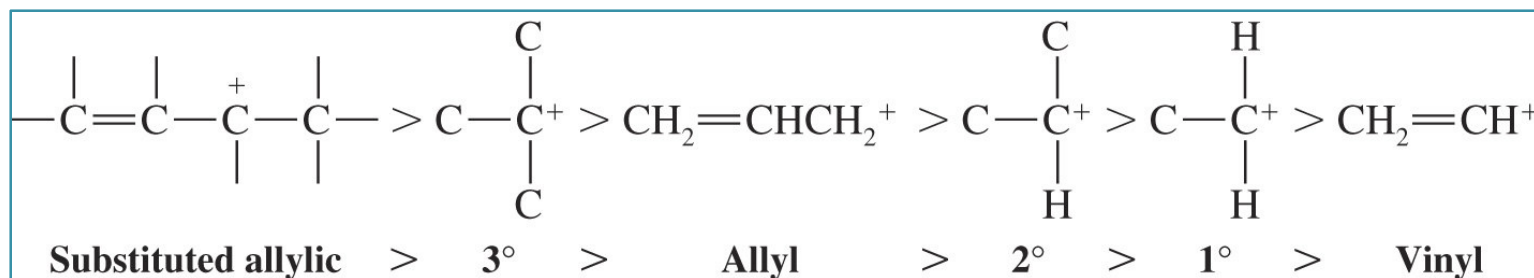
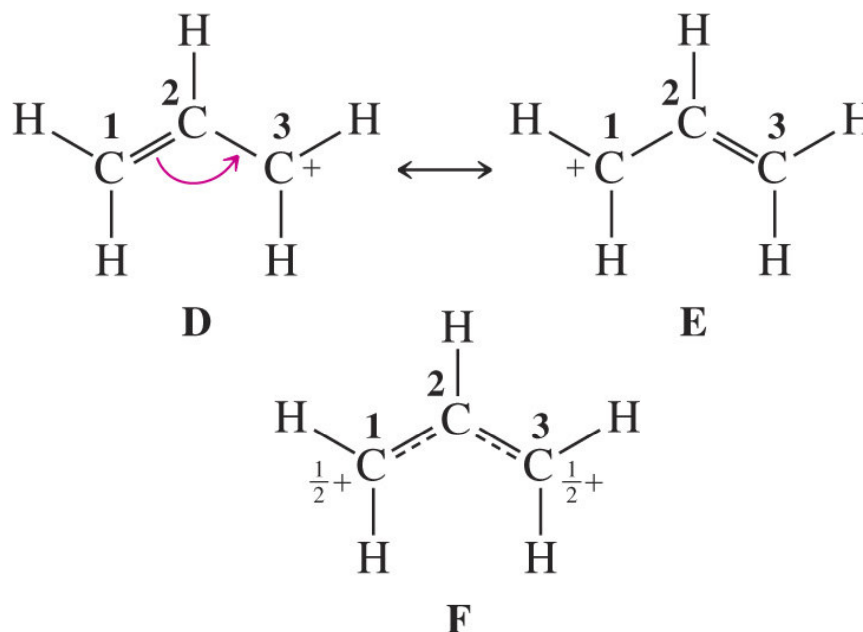


- In step 2 chloride can react at either end of the allyl cation
 - This leads to either 1,2 or 1,4 product

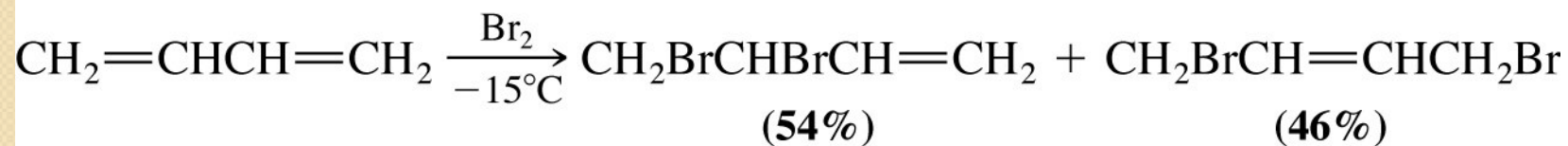
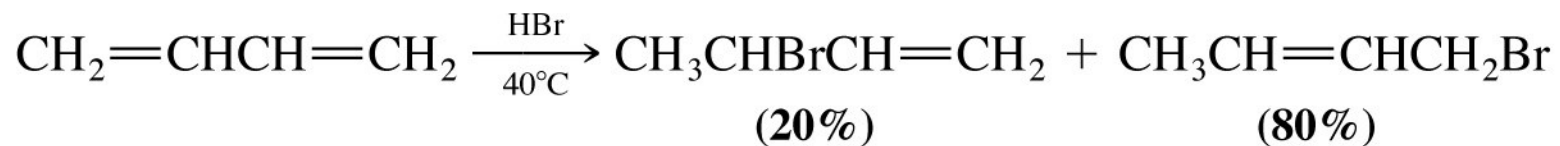


Relative Stability of Allylic Carbocation

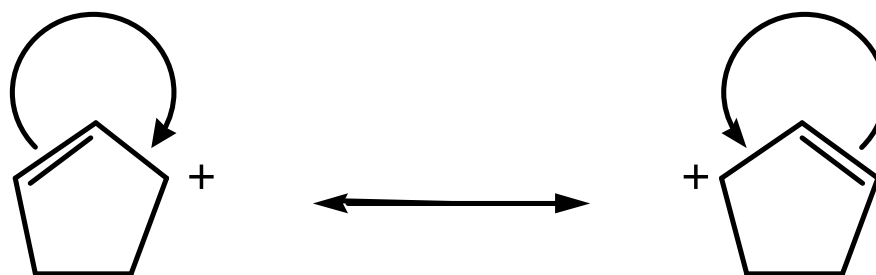
- Resonance theory predicts that the allyl cation is a hybrid of equivalent structures D and E
 - Both molecular orbital theory and resonance theory suggest that structure F is the best representation for the allyl cation



Other electrophilic reagents add to conjugated dienes in similar fashion

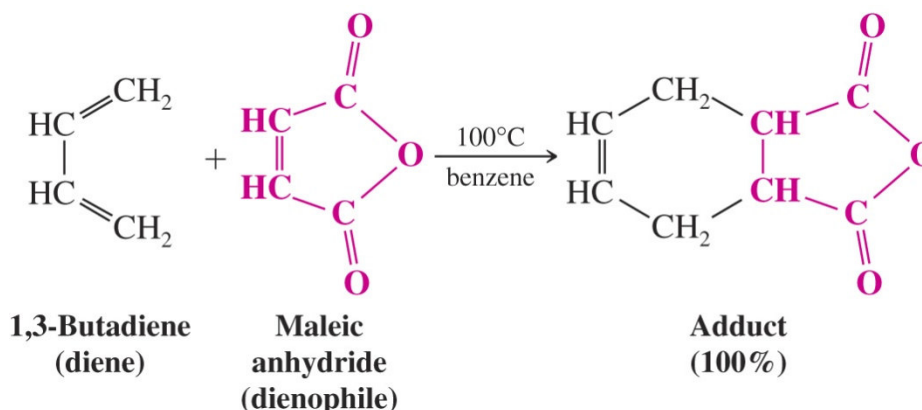


Problem 3.23: The resonance hybrid structure of the 3-cyclopentenyl cation

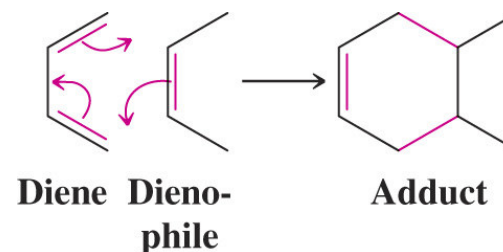


3.15.b Cycloaddition to Conjugated Dienes: The Diels-Alder Reaction

- The Diels-Alder Reaction: A 1,4-Cycloaddition Reaction of Dienes
 - Heating 1,3-butadiene and maleic anhydride gives a 6-membered ring product in 100% yield

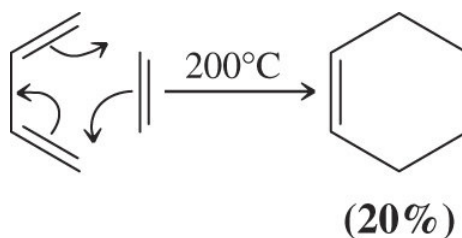


- The general Diels-Alder reaction forms a cyclohexene product
 - Overall, two new σ bonds are formed at the expense of two π bonds
 - The conjugated diene is a 4π -electron system
 - The dienophile ("diene lover") is a 2π -electron system
 - The product is called an adduct

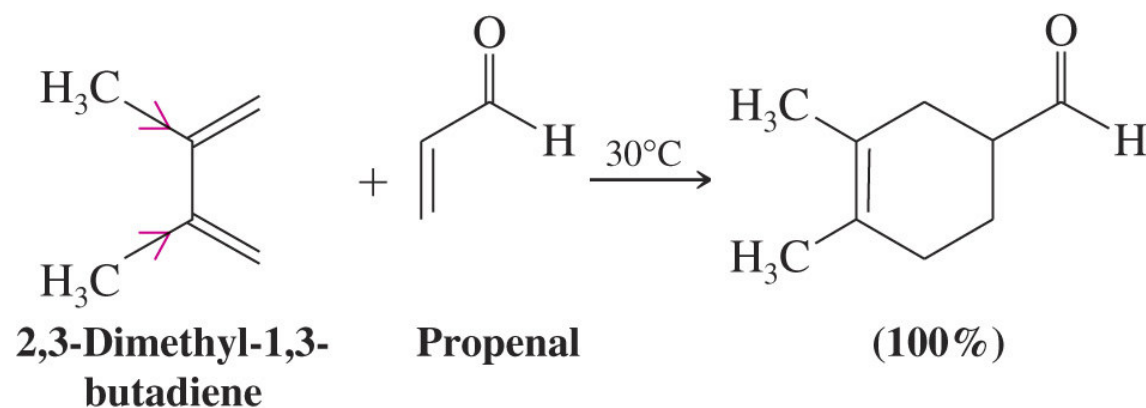


◦ **Factors Favoring the Diels-Alder Reaction**

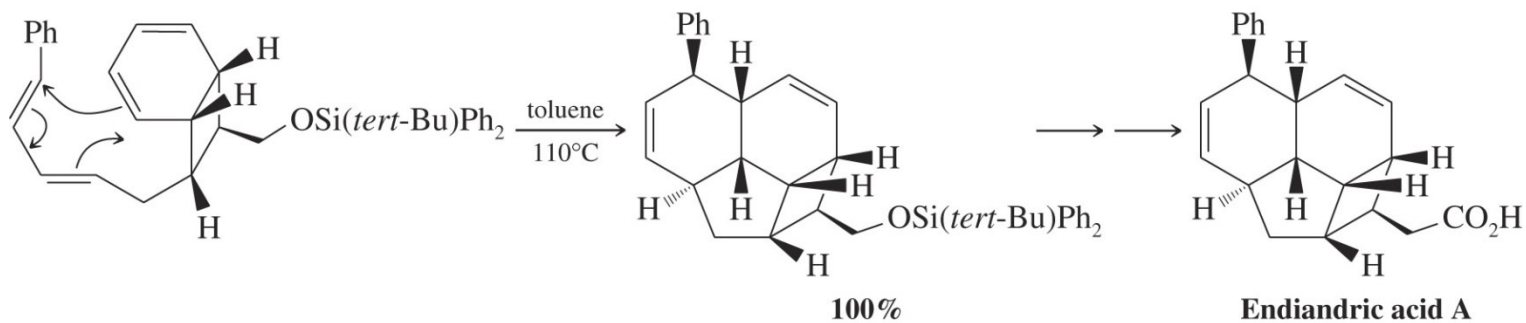
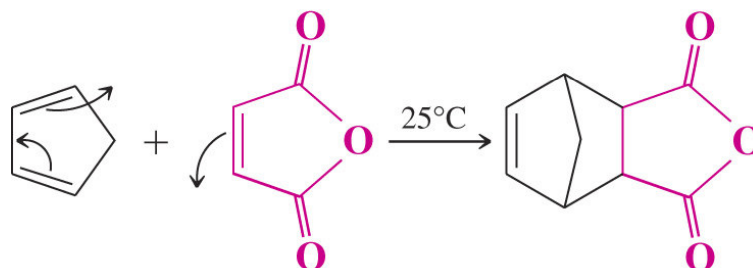
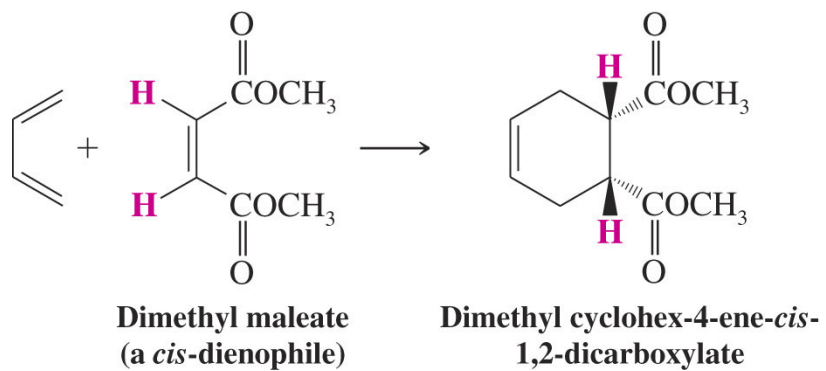
- The simplest possible example of a Diels-Alder reaction goes at very low yield and requires high temperatures



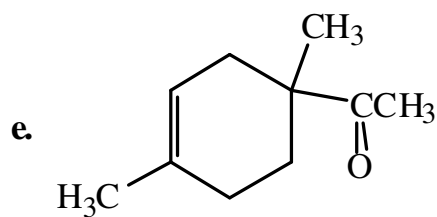
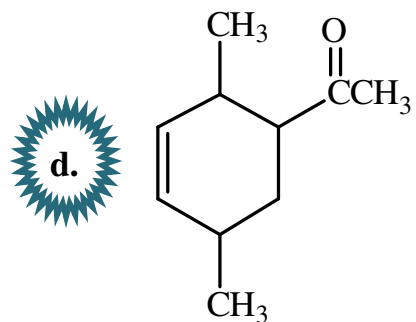
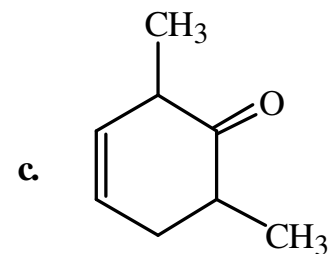
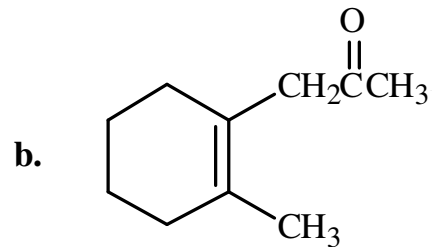
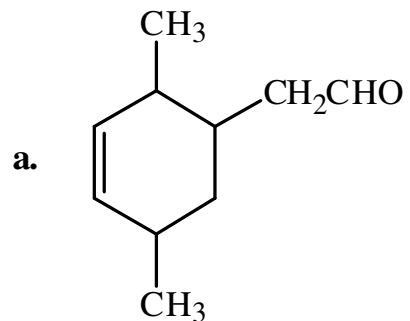
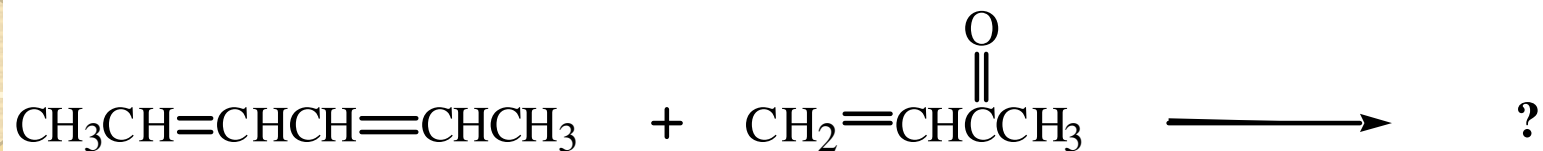
- To proceed in good yield and at low temperature the dienophile should have electron-withdrawing groups
 - It also helps if the diene has electron-releasing groups
 - Dienes with electron-donating groups and dienophiles with electron-withdrawing group can also react well together

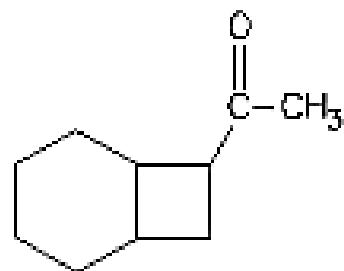
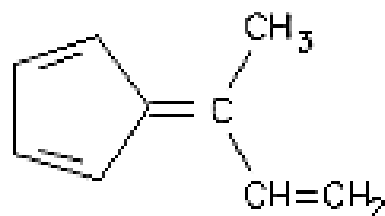
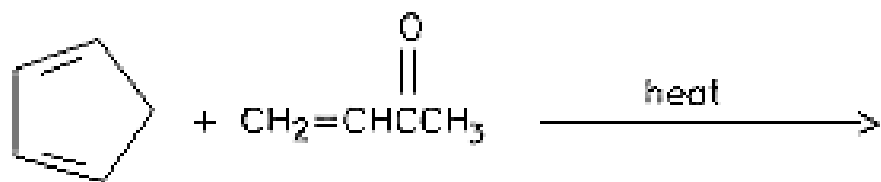


Examples

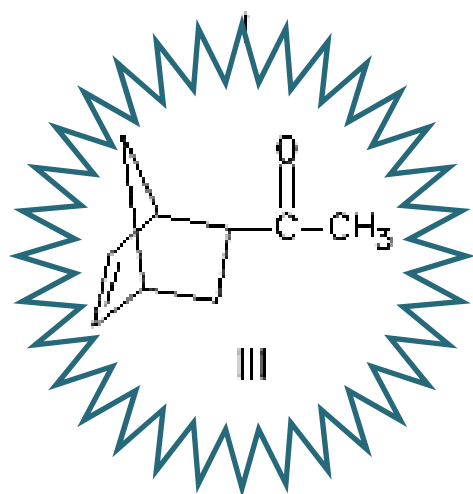


Questions

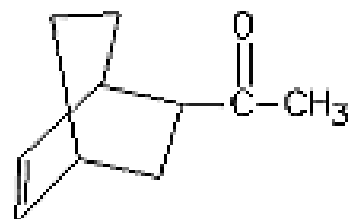




II



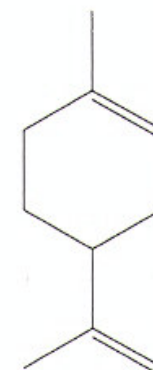
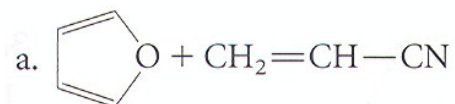
III



IV

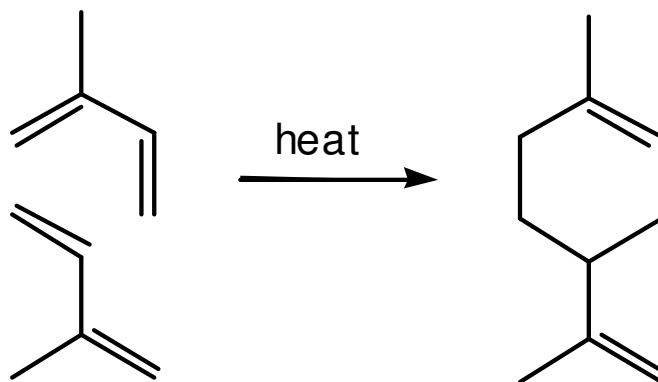
PROBLEM 3.25 Show how limonene (Figure 1.13) could be formed by a Diels–Alder reaction of isoprene (2-methyl-1,3-butadiene) with itself.

PROBLEM 3.26 Draw the structure of the product of each of the following cycloaddition reactions.

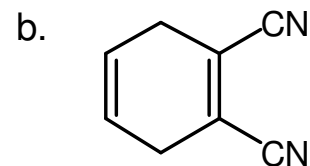
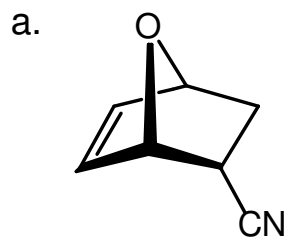


limonene
(citrus fruit oils)
bp 178°C

3.25



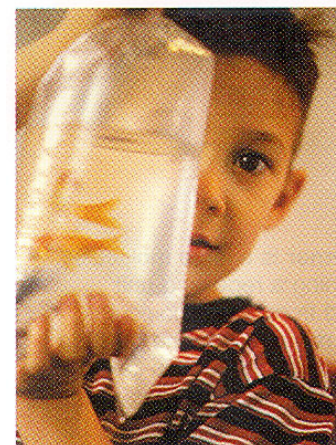
3.26



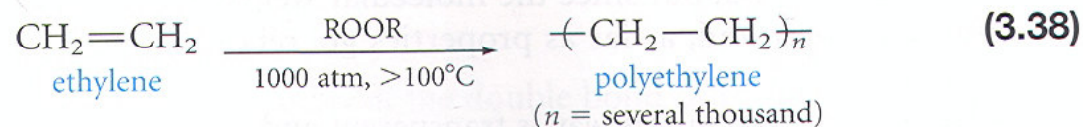
3.16

Free-Radical Additions; Polyethylene

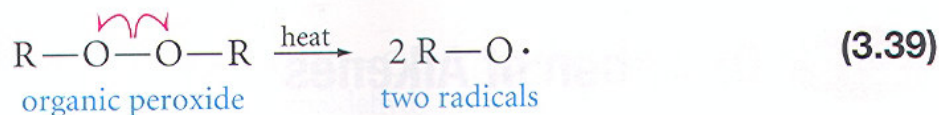
A **polymer** is a large molecule containing a repeating unit derived from small molecules called **monomers**. The process of polymer formation is called **polymerization**.



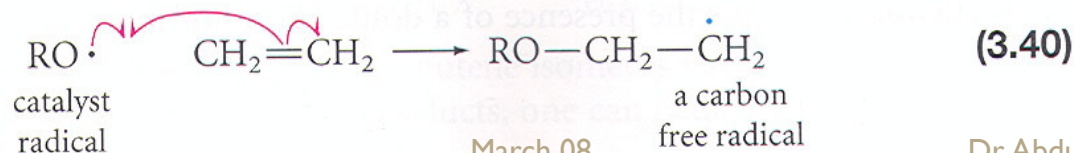
The free-radical polymerization of ethylene gives **polyethylene**, a material that is produced on a very large scale (more than 8 billion pounds annually in the United States alone). The reaction is carried out by heating ethylene under pressure with a catalyst (eq. 3.38). How does this reaction occur?



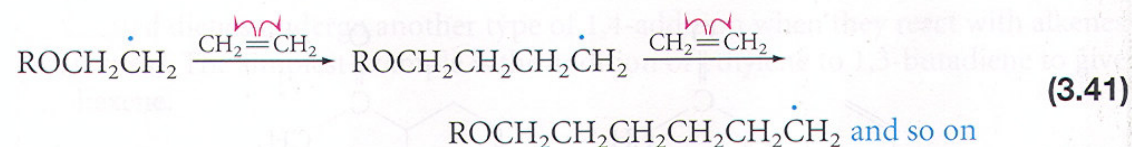
One common type of catalyst for polymerization is an organic peroxide. The O—O single bond is weak, and on heating this bond breaks, with one electron going to each of the oxygens.



A catalyst radical then adds to the carbon-carbon double bond:

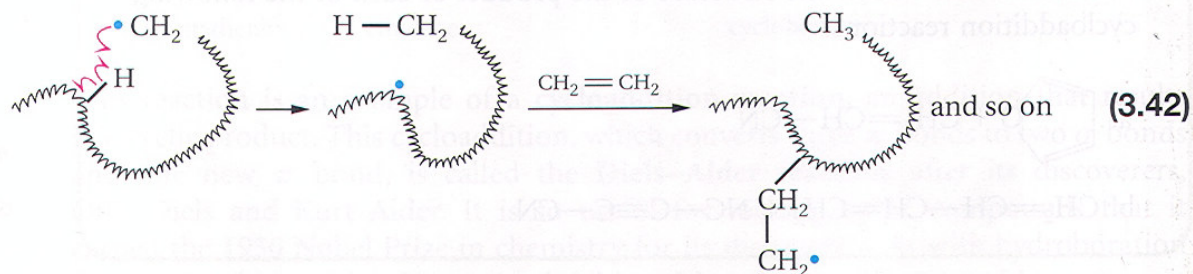


The result of this addition is a carbon free radical, which may add to another ethylene molecule, and another, and another, and so on.

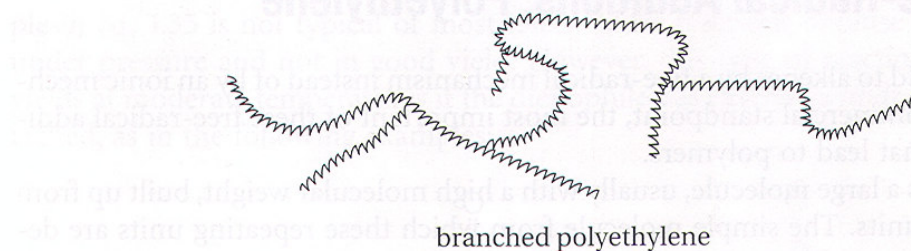


The carbon chain continues to grow in length until some chain-termination reaction occurs (perhaps a combination of two radicals).

We might think that only a single long chain of carbons will be formed in this way, but this is not always the case. A “growing” polymer chain may abstract a hydrogen atom from its back, so to speak, to cause **chain branching**.



A giant molecule with long and short branches is thus formed:

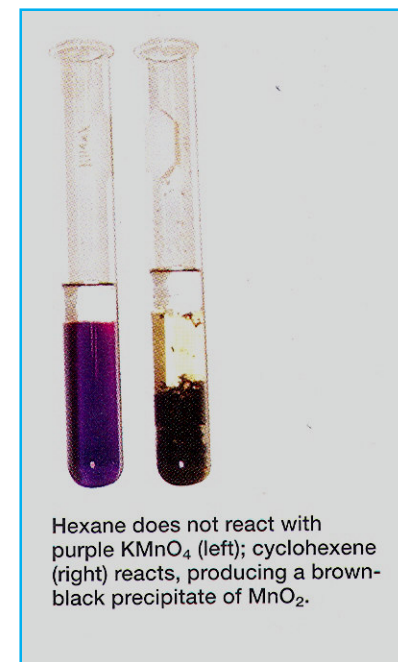
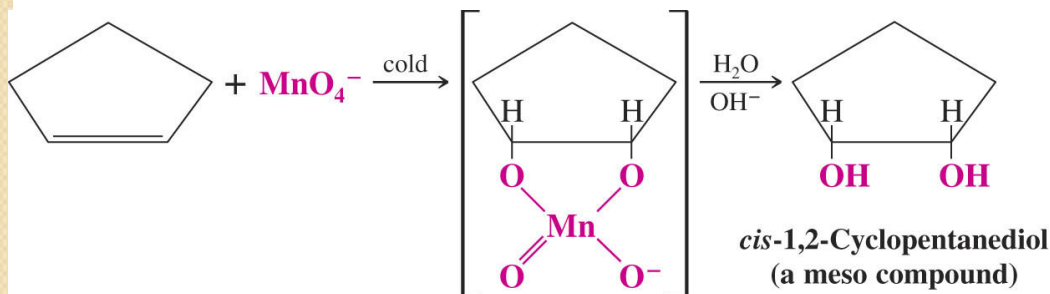
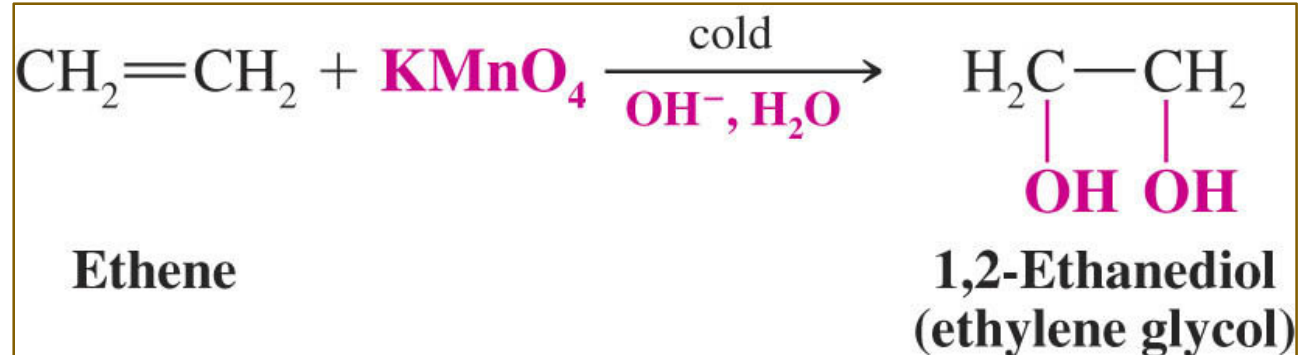


3.17



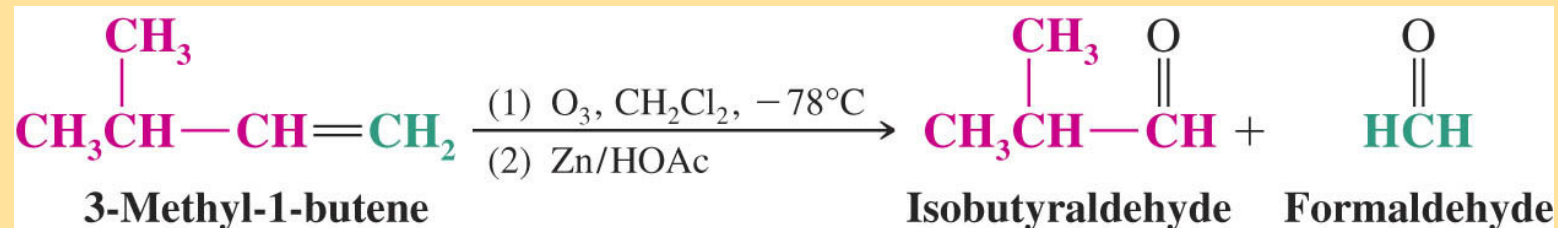
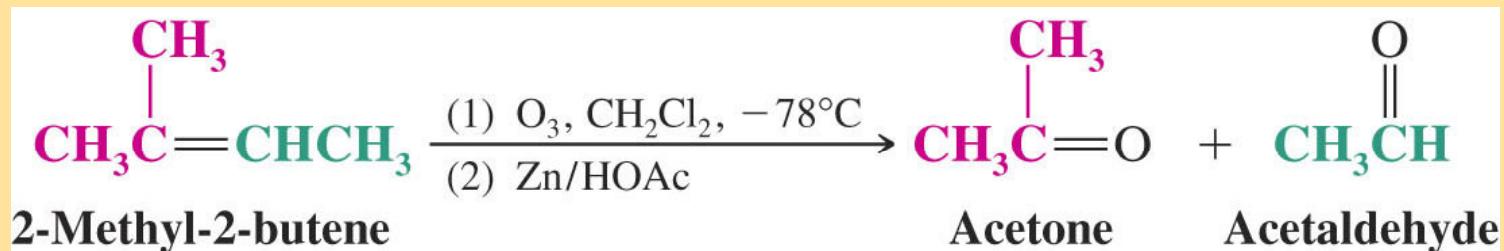
OXIDATION OF ALKENES

3.17.a Oxidation with Permanganate; a Chemical Test

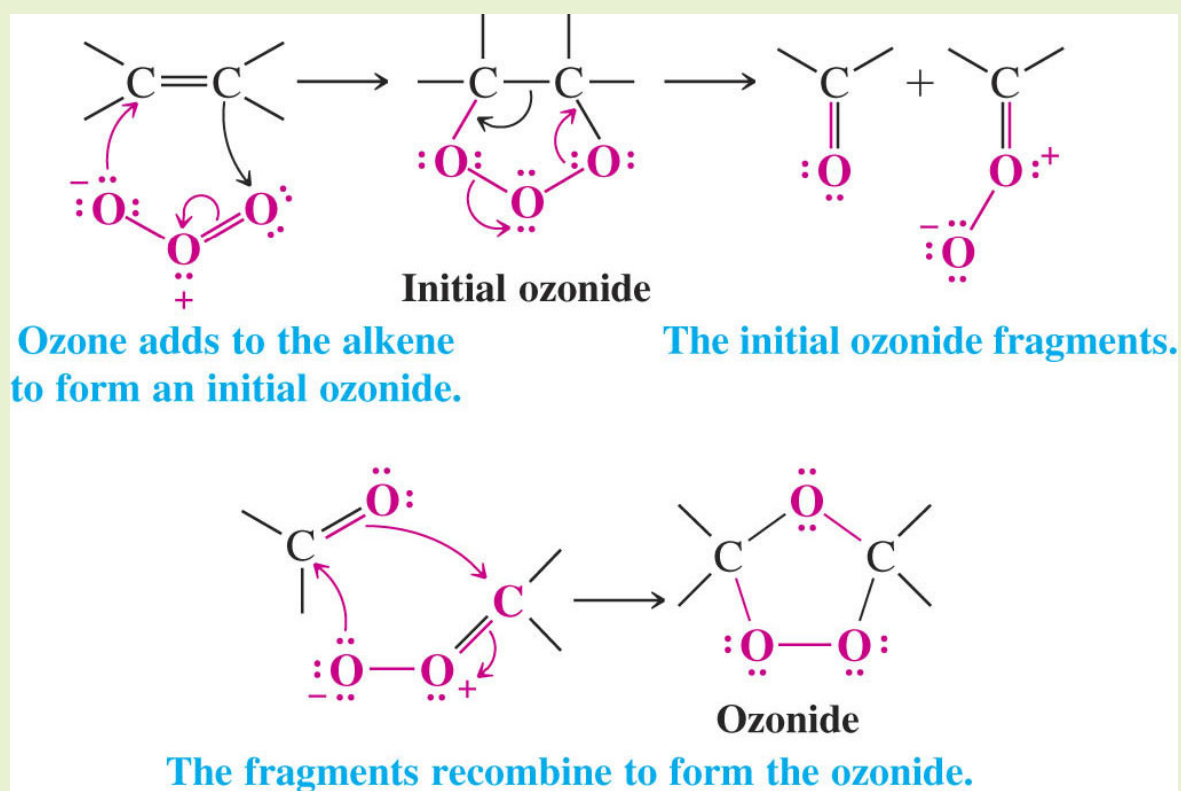


3.17.b Ozonolysis of Alkenes

Cleavage of alkenes with ozone and workup with zinc in acetic acid leads to less highly oxidized carbons than products from cleavage with hot KMnO_4 . Unsubstituted carbons are oxidized to formaldehyde, monosubstituted carbons are oxidized to aldehydes and disubstituted carbons are oxidized to ketones.

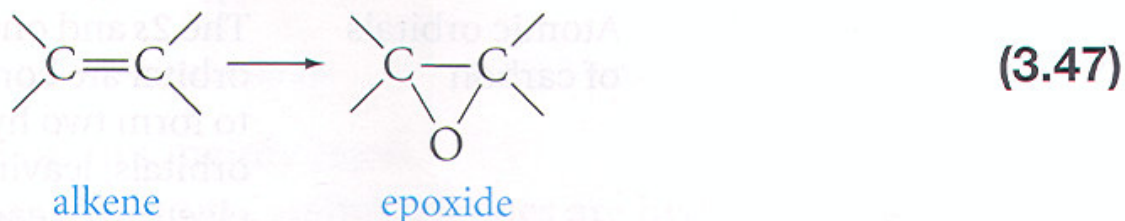


Ozone adds across the double bond to form the initial ozonide which rearranges to a highly unstable ozonide
 The ozonides react with zinc and acetic acid to effect the cleavage



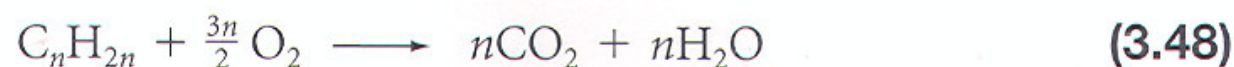
3.17.c Other Alkene Oxidations

Various reagents can convert alkenes to epoxides (eq. 3.47).



This reaction and the chemistry of epoxides are detailed in Chapter 8.

Like alkanes (and all other hydrocarbons), alkenes can be used as fuels. Complete combustion gives carbon dioxide and water.

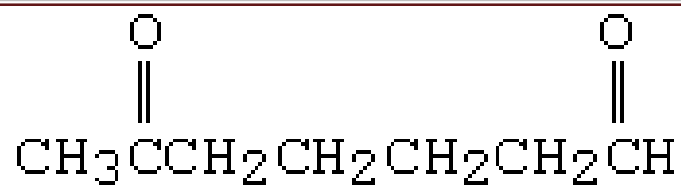


Examples

PROBLEM 3.28 Which alkene will give only acetone, $(\text{CH}_3)_2\text{C}=\text{O}$, as the ozonolysis product?



Compound, C, has the molecular formula C_7H_{12} . On catalytic hydrogenation, 1 mol of C absorbs 1 mol of hydrogen and yields a compound with the molecular formula C_7H_{14} . On ozonolysis and subsequent treatment with zinc and acetic acid, C yields only:



The structure of C is:

