



Chapter 3

Dienes

3.1 Introduction

Dienes are simply alkenes that contain two carbon-carbon double bonds. They therefore have essentially the same properties as the alkenes we have already studied. For certain of the dienes, these alkene properties are modified in important ways; we shall focus our attention on these modifications.

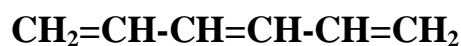
Dienes are named by the IUPAC system in the same way as alkenes, except that the ending **-diene** is used, with two numbers to indicate the position of the two double bonds. This system is easily extended to compounds containing any number of double bonds.



1,3-Butadiene

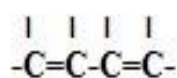


1,4-Pentadiene



1,3,5-Hexatriene

Dienes are divided into two important classes according to the arrangement of the double bonds. Double bonds that alternate with single bonds are said to be conjugated; double bonds that are separated by more than one single bond are said to be isolated.

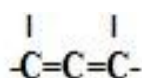


Conjugated
double bonds



Isolated
double bonds

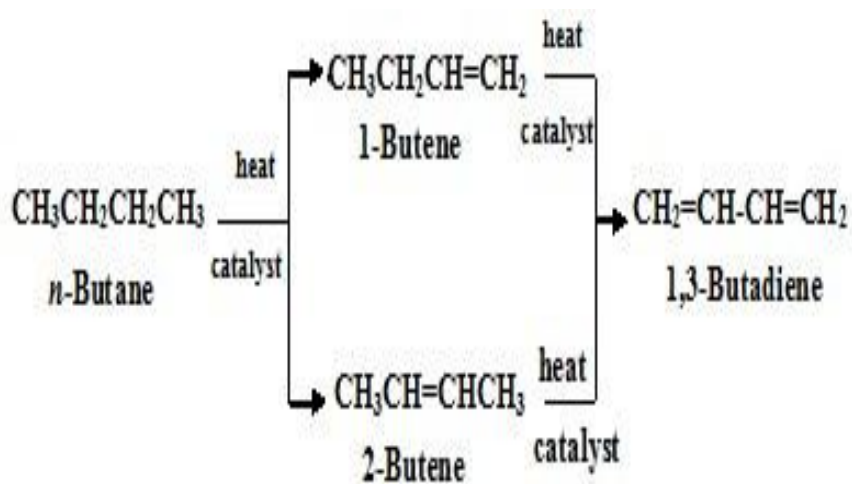
A third class of dienes, of increasing interest to organic chemists, contains cumulated double bonds; these compounds are known as allenes;

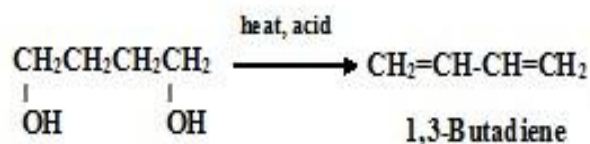


Cumulated double bonds: allenes

3.2 Preparation and Properties of Dienes

Dienes are usually prepared by adaptations of the methods used to make simple alkenes. For example, the most important diene, 1,3-butadiene (used to make synthetic rubber), has been made by cracking process, or by dehydration of an alcohol containing two –OH groups:



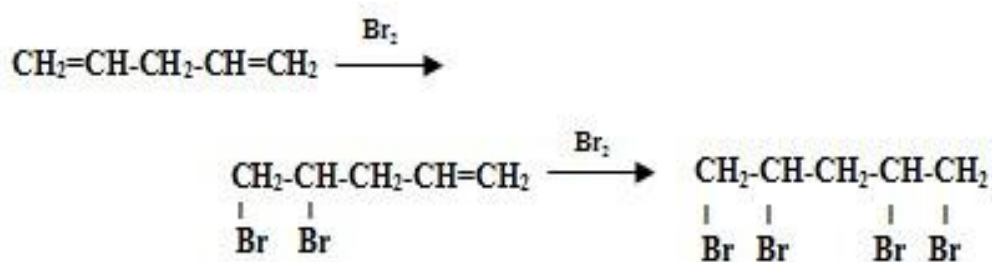


The chemical properties of a diene depend upon the arrangement of its double bonds. Isolated double bonds exert little effect on each other, and hence each reacts as though it were the only double bond in the molecule. Except for the consumption of larger amounts of reagents, then, the chemical properties of the non-conjugated dienes are identical with those of the simple alkenes.

Conjugated dienes differ from simple alkenes in three ways: (a) they are more stable, (b) they undergo 1,4-addition, and (c) toward free radical addition, they are more reactive.

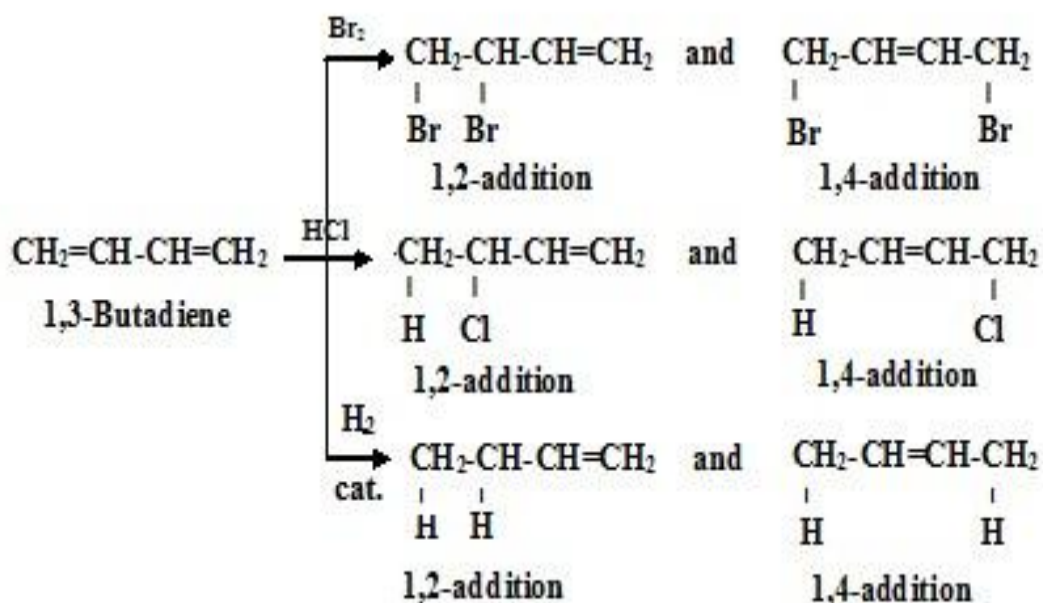
3.3-(Reaction) Electrophilic Addition to Conjugated dienes, 1,4-Addition

When 1,4-Pentadiene is treated with bromine under conditions that favor formation of the dihalide, there is obtained the expected product, 4,5-dibromo-1-pentene. Addition of more bromine yields the 1,2,4,5-tetrabromopentane.



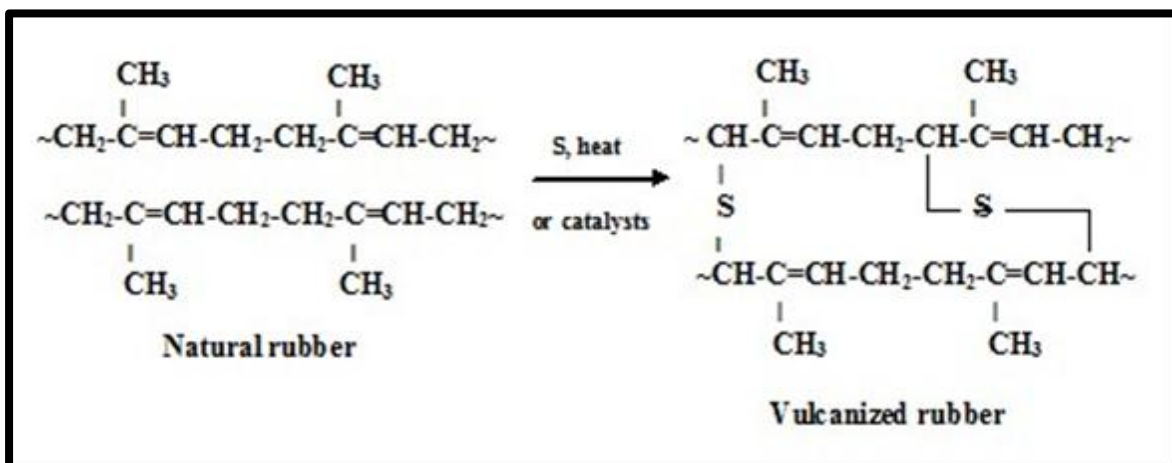
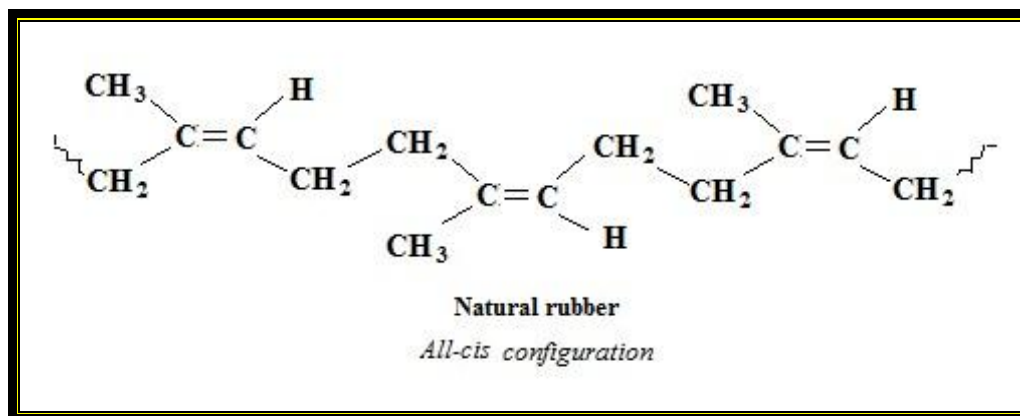
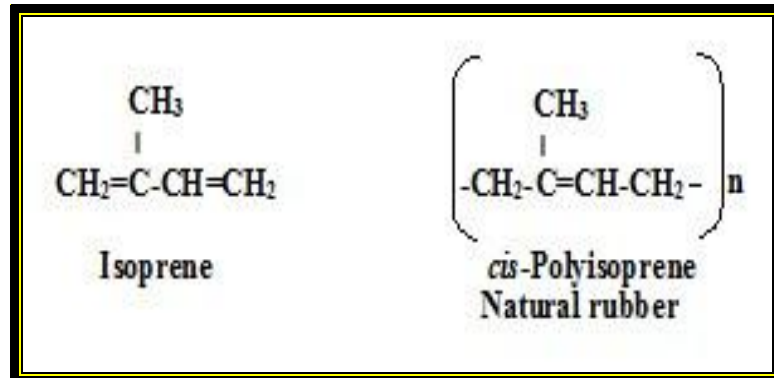
This is typical of the behavior of dienes containing isolated double bonds: the double bonds react independently, as though they were in different molecules.

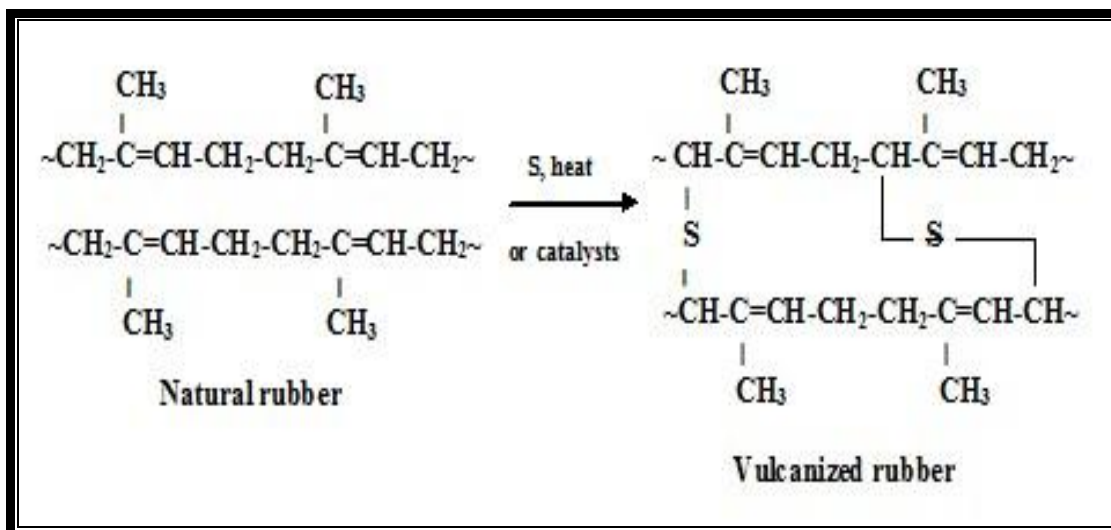
When 1,3-butadiene is treated with bromine under similar conditions, there is obtained not only the expected 3,4-dibromo-1-butene, but also 1,4-dibromo-2-butene. Treatment with HCl yields not only 3-chloro-1-butene, but also 1-chloro-2-butene. Hydrogenation yields not only 1-butene but also 2-butene.



Study of many conjugated dienes and many reagents shows that such behavior is typical: in addition to conjugated dienes, a reagent may attach itself not only to a pair of adjacent carbons (1,2-addition), but also to the carbons at the two ends of the

conjugated system (1,4-addition). Very often the 1,4-addition product is the major one.





3.4 Analysis of Dienes:

Dienes respond to characterization tests in the same way as alkenes, they decolorize bromine in carbon tetrachloride without evolution of hydrogen bromide, and they decolorize cold, neutral, dilute permanganate; they are not oxidized by chromic anhydride. They are, however, more unsaturated than alkenes.

Ozonolysis of dienes yields aldehydes and ketones, including double-ended ones containing two C=O groups per molecule. For example:

