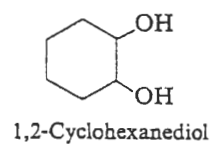
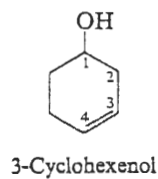
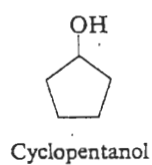
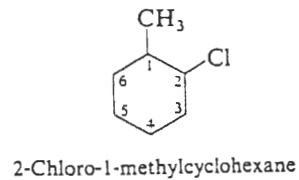
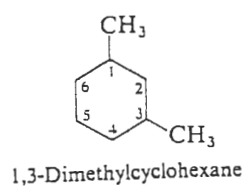
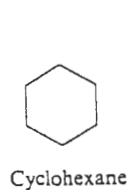
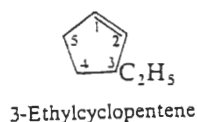
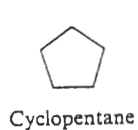
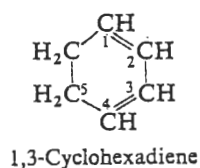
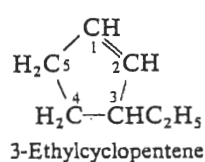
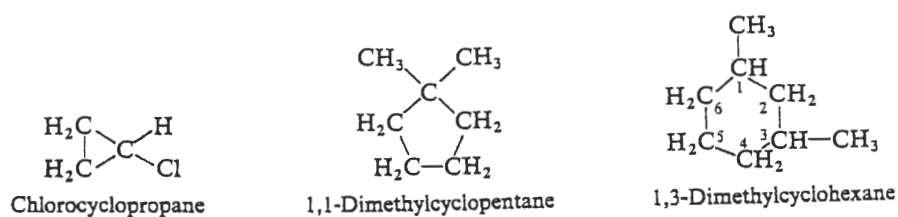


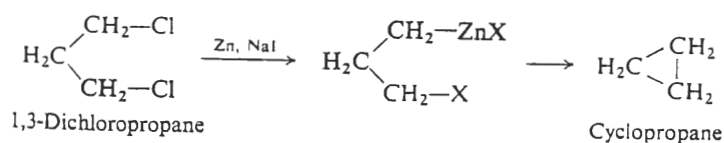
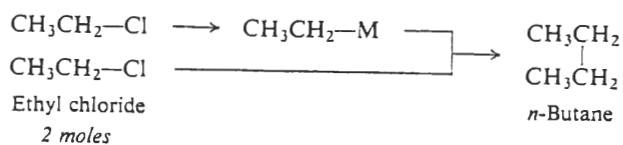
Cyclic Aliphatic Compounds

Nomenclature

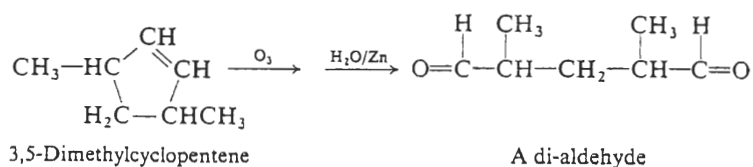
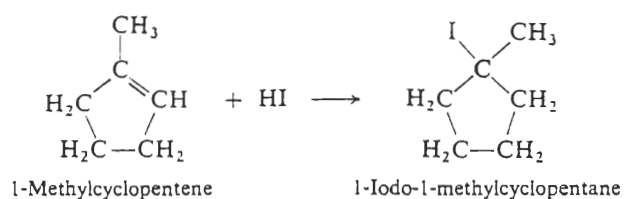
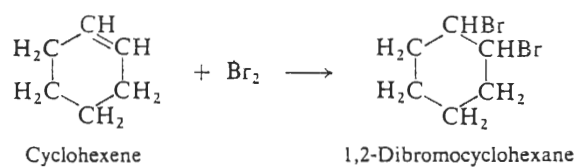
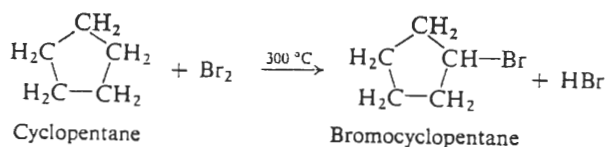
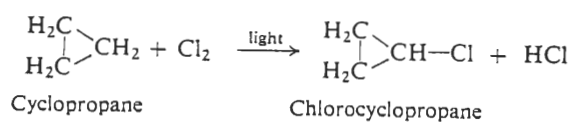
Cyclic aliphatic hydrocarbons are named by prefixing **cyclo-** to the name of the corresponding open-chain hydrocarbon having the same number of carbons as the ring.



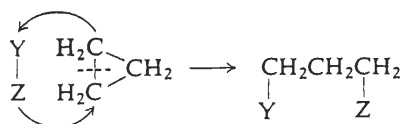
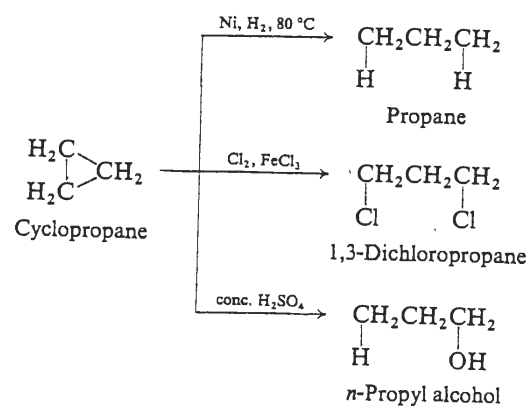
Preparation



Reactions



Reactions of small-ring compounds. Cyclopropane and cyclobutane



HEATS OF COMBUSTION OF CYCLOALKANES

Ring size	Heat of combustion per CH ₂ , kcal/mol	Ring size	Heat of combustion per CH ₂ , kcal/mol
3	166.6	10	158.6
4	164.0	11	158.4
5	158.7	12	157.6
6	157.4	13	157.8
7	158.3	14	157.4
8	158.6	15	157.5
9	158.8	17	157.2
		Open-chain 157.4	

Factors affecting stability of conformations

To go more deeply into the chemistry of cyclic compounds, we must use conformational analysis. As preparation for that, let us review the factors that determine the stability of a conformation.

Any atom tends to have bond angles that match those of its bonding orbitals: tetrahedral (109.5°) for *sp*³-hybridized carbon, for example. Any deviations from the "normal" bond angles are accompanied by **angle strain**.

Any pair of tetrahedral carbons attached to each other tend to have their bonds staggered. That is to say, any ethane-like portion of a molecule tends, like ethane, to take up a staggered conformation. Any deviations from the staggered arrangement are accompanied by **torsional strain**.

Any two atoms (or groups) that are not bonded to each other can interact in several ways, depending on their size and polarity, and how closely they are brought together. These non-bonded interactions can be either repulsive or attractive, and the result can be either destabilization or stabilization of the conformation.

Non-bonded atoms (or groups) that just touch each other—that is, that are about as far apart as the sum of their van der Waals radii—attract each other. If brought any closer together, they repel each other: such crowding together is accompanied by **van der Waals strain (steric strain)**.

Non-bonded atoms (or groups) tend to take positions that result in the most favorable **dipole–dipole interactions**: that is, positions that minimize dipole–dipole repulsions or maximize dipole–dipole attractions. (A particularly powerful attraction results from the special kind of dipole–dipole interaction called the **hydrogen bond**.)

All these factors, working together or opposing each other, determine the net stability of a conformation. To figure out what the most stable conformation of a particular molecule should be, one ideally should consider all possible combinations of bond angles, angles of rotation, and even bond lengths, and see which combination results in the lowest energy content. Such calculations have become quite feasible through the use of computers.

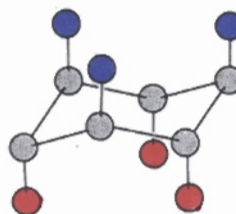
Both calculations and experimental measurements show that the final result is a compromise, and that few molecules have the idealized conformations that we assign them and, for convenience, usually work with. For example, probably no tetravalent carbon compound—except one with four identical substituents—has *exactly* tetrahedral bond angles: a molecule accepts a certain amount of angle strain to relieve van der Waals strain or dipole–dipole interaction. In the *gauche* con-

former of *n*-butane the dihedral angle between the methyl groups is not 60° , but almost certainly larger: the molecule accepts some torsional strain to ease van der Waals strain between the methyl groups.

Conformations of cycloalkanes

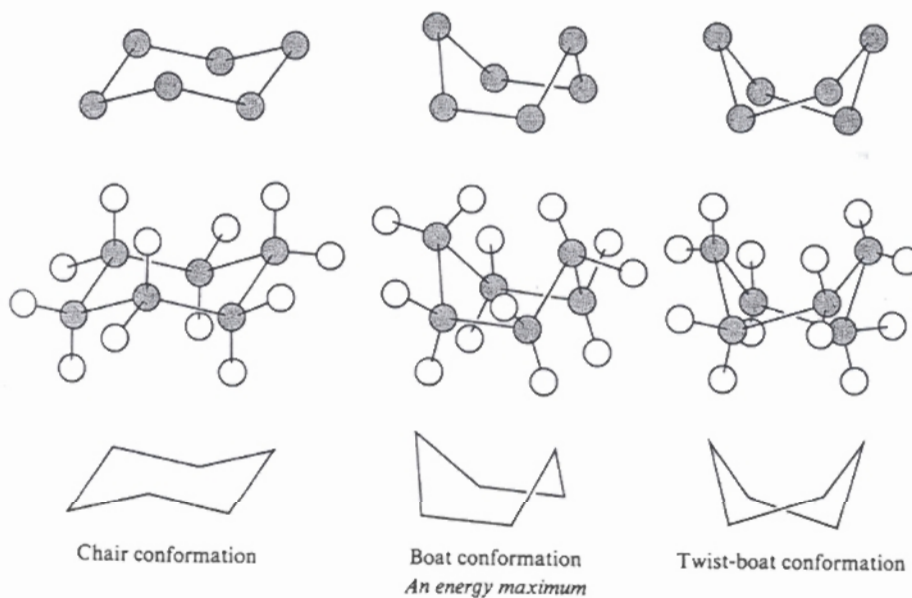


Equatorial bonds



Axial bonds

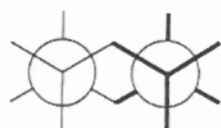
Chair cyclohexane: equatorial and axial bonds.



Chair conformation

Boat conformation
An energy maximum

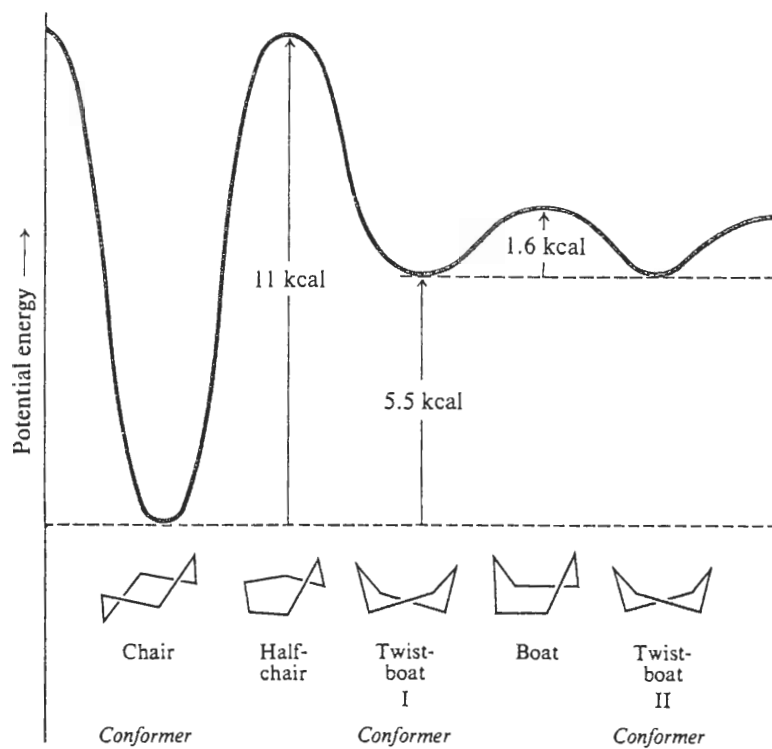
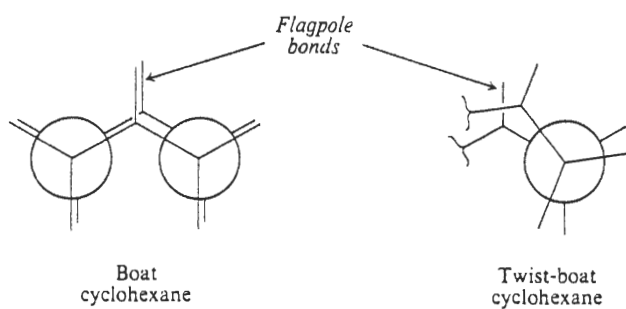
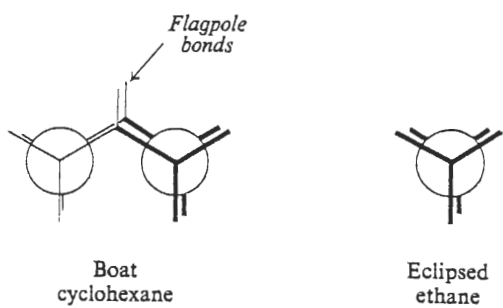
Twist-boat conformation



Chair
cyclohexane

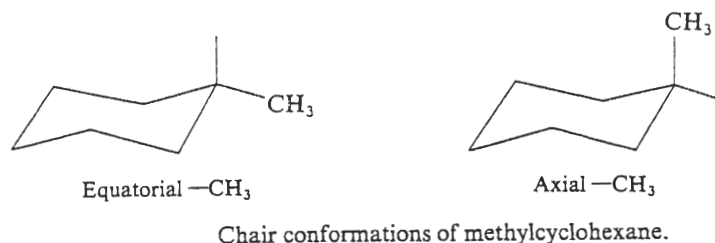


Staggered
ethane



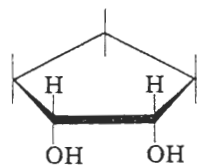
Potential energy relationships among conformations of cyclohexane.

If, now, a hydrogen is replaced by a larger atom or group, crowding occurs. The most severe crowding is among atoms held by the three axial bonds on the same side of the molecule; the resulting interaction is called **1,3-diaxial interaction**. Except for hydrogen, a given atom or group has more room in an equatorial position than in an axial position.

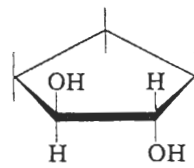


Stereoisomerism of cyclic compounds: *cis* and *trans* isomers

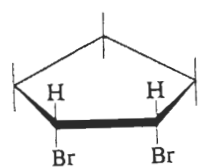
Let us turn for the moment from conformational analysis, and look at configurational isomerism in cyclic compounds.



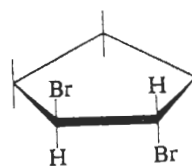
I
cis-1,2-Cyclopentanediol



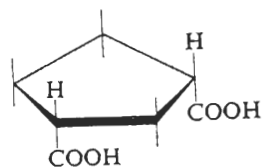
II
trans-1,2-Cyclopentanediol



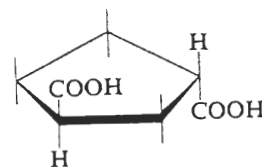
cis-1,2-Dibromocyclopentane



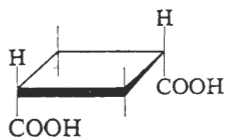
trans-1,2-Dibromocyclopentane



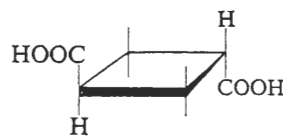
cis-1,3-Cyclopentanedicarboxylic acid



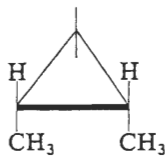
trans-1,3-Cyclopentanedicarboxylic acid



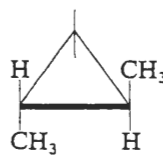
cis-1,3-Cyclobutanedicarboxylic acid



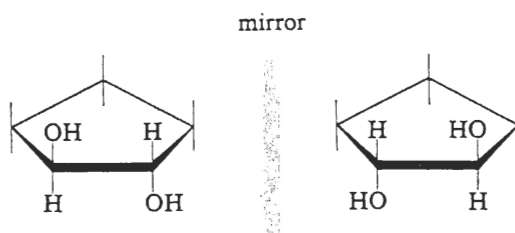
trans-1,3-Cyclobutanedicarboxylic acid



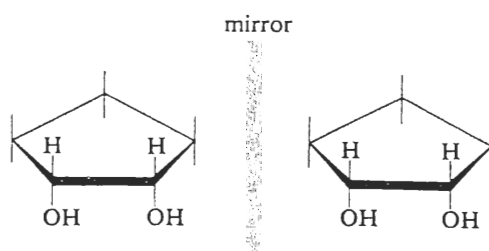
cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane

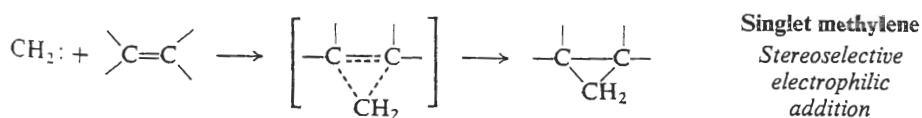
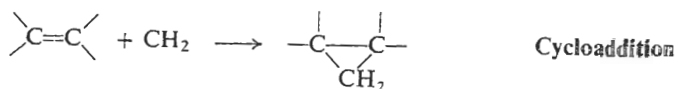
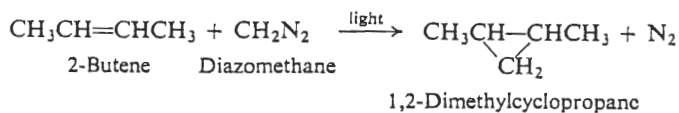
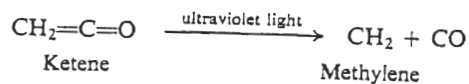
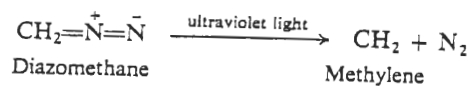


Not superimposable
Enantiomers: resolvable
trans-1,2-Cyclopentanediol

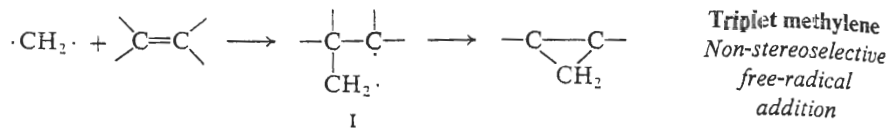


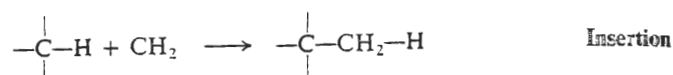
Superimposable
A meso compound
cis-1,2-Cyclopentanediol

Carbenes. Methylene. Cycloaddition



It is **triplet** methylene that undergoes the *non-stereoselective addition*. Triplet methylene is a diradical, and it adds by a *free-radical two-step mechanism*: actually,

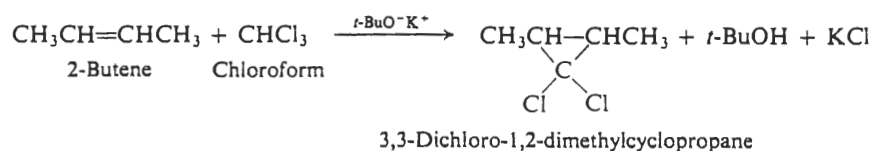




Addition of substituted carbenes. 1,1-Elimination

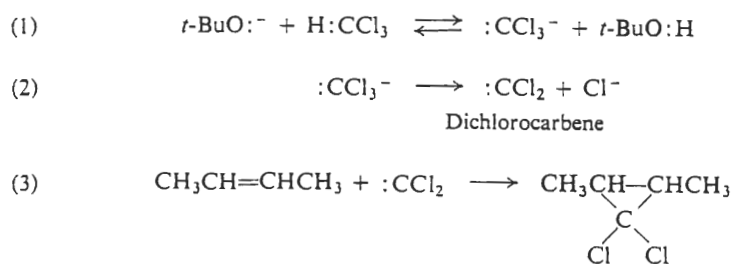
The addition of carbenes to alkenes is used principally to make cyclopropanes. For this purpose one seldom uses methylene itself, but rather various substituted carbenes. These are often generated in ways quite different from the photochemical reactions described in the preceding section.

A common method for making cyclopropanes is illustrated by the reaction of 2-butene with chloroform in the presence of potassium *tert*-butoxide:

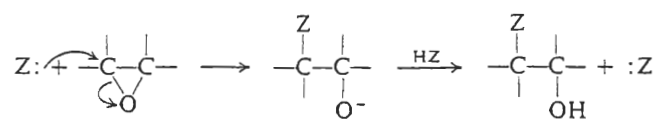
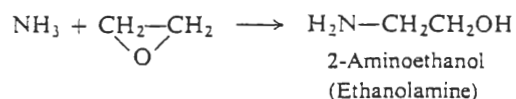
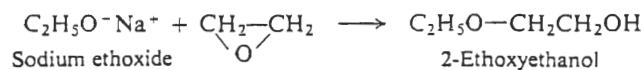


The dichlorocyclopropanes obtained can be reduced to hydrocarbons or hydrolyzed to *ketones*, the starting point for many syntheses

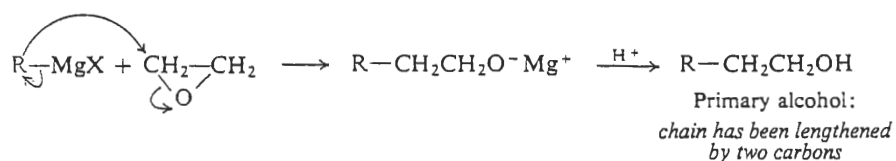
Here, too, reaction involves a divalent carbon compound, a derivative of methylene: *dichlorocarbene*, $:\text{CCl}_2$. It is generated in two steps, initiated by attack on chloroform by the very strong base, *tert*-butoxide ion, and then adds to the alkene.



2. Base-catalyzed cleavage.

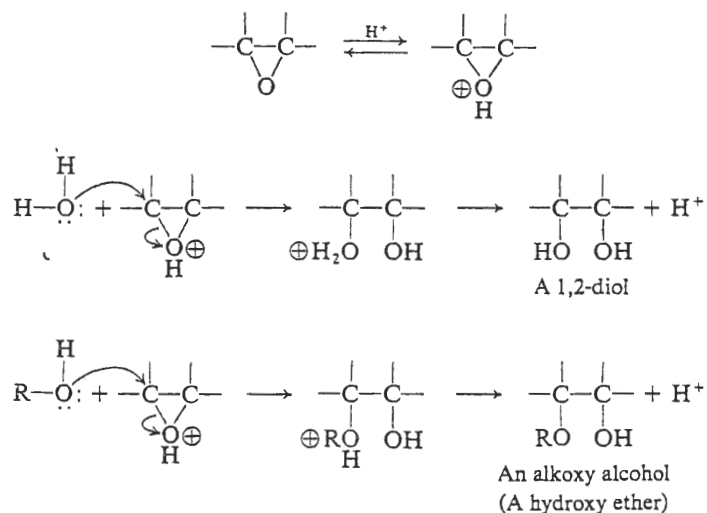
*Examples:*

3. Reaction with Grignard reagents.

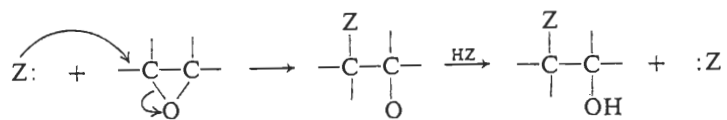
**Acid-catalyzed cleavage of epoxides. *anti*-Hydroxylation**

Like other ethers, an epoxide is protonated by acid; the protonated epoxide can then undergo attack by any of a number of nucleophilic reagents.

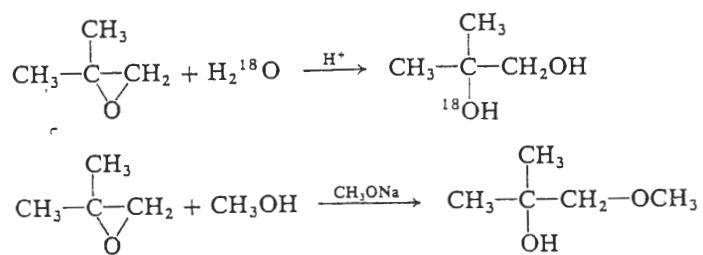
An important feature of the reactions of epoxides is the formation of compounds that contain *two* functional groups. Thus, reaction with water yields a 1,2-diol; reaction with an alcohol yields a compound that is both ether and alcohol.



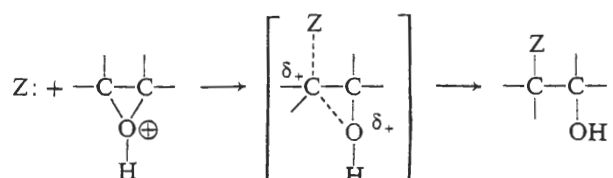
Base-catalyzed cleavage of epoxides



Orientation of cleavage of epoxides

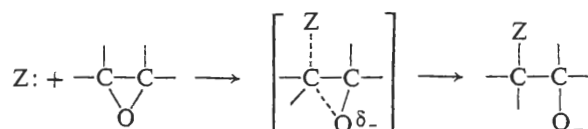


Acid-catalyzed S_N2 cleavage



*Bond-breaking exceeds
bond-making:
positive charge on carbon*

Base-catalyzed S_N2 cleavage



*Bond-making balances
bond-breaking:
no particular charge
on carbon*