Carbocyclic Rings

Paper 4201 B

Organic Chemistry
(Special-II)

Classification of monocyclic compounds (*on the basis of number of carbon atoms in the ring*):
3-4 C-atoms: **Small rings**
5-7 C-atoms: **Normal rings**
8-11 C-atoms: **Medium rings**
>12 C-atoms: **Large rings**

Baeyer Theory on the Strain in Cycloalkane Rings

Baeyer, suggested that cyclopropane and cyclobutane are less stable than cyclohexane, because the smaller rings are more "strained". sp^3 hybridized carbons in cycloalkanes do not have the expected ideal bond angle of 109.5° this causes strain in the molecule (**Angle Strain**).

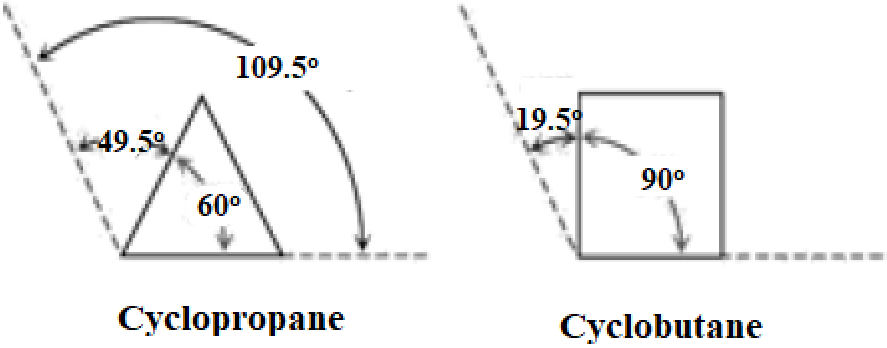


Figure: Deviation from ideal bond angle of 109.5°

- The deviation is higher for cyclopropane than cyclobutane therefore cyclopropane is more prone to undergo ring opening reactions.

- Baeyer's theory is based upon some assumptions that all ring systems are planar. Deviation from normal tetrahedral angles results in unstable cycloalkanes.

- However, contrary to the Bayer's theory, the bond angles in cyclohexane and higher cycloalkanes are not larger than 109.5° because the carbon rings of those compounds are not planar but they are puckered.

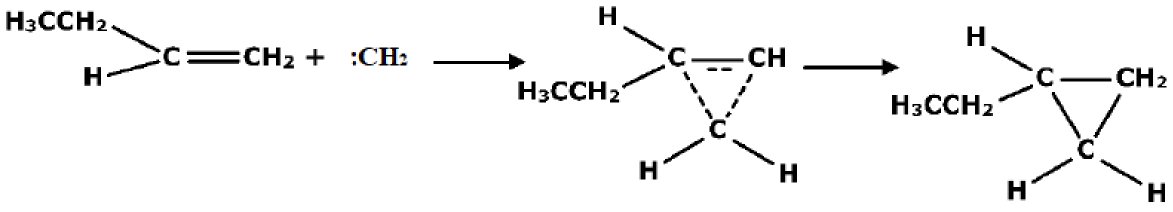
- Strain in small-ring cycloalkanes affect their physical and chemical properties. Cyclopropane and cyclobutane undergo C−C bond cleavage reactions, like alkenes, that are not observed for cyclopentane and cyclohexane, or for saturated, open-chain hydrocarbons.

Cyclopropanes

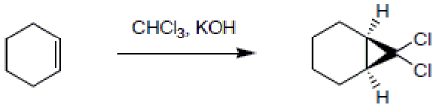
- Stable but highly strained compounds (ring strain ~29 kcal/mol).
- C–C bond angles = 60°
- Substituents on cyclopropanes are eclipsed. H–C–H angle is ~120°. As a result, the C–H bonds have higher s character compared to normal sp_3 bonds.
- Highly strained cyclopropane ring shows reactivity analogous to that of alkenes than that of alkanes.

Some General Strategies for Cyclopropanation

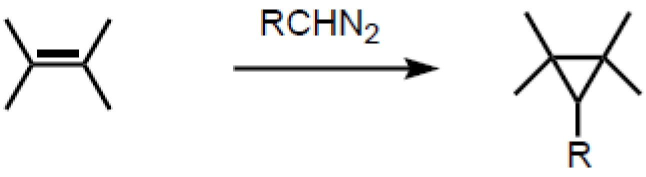
1. BY REACTION OF AN ALKENES WITH A CARBENE



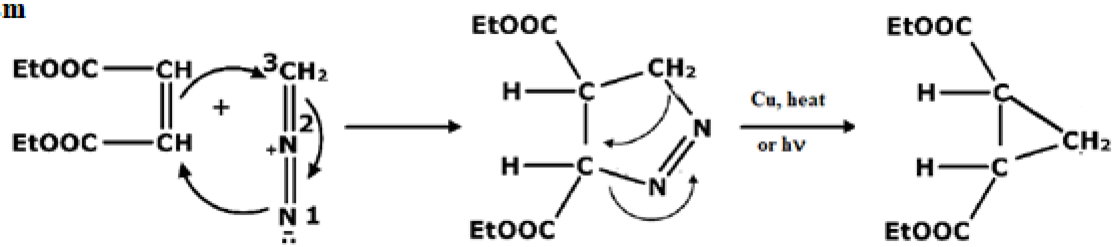
$$CHCl_3 + KOH \longrightarrow Cl_2C: + H_2O + KCl$$



2. VIA CARBENES GENERATED BY DECOMPOSITION OF DIAZO COMPOUNDS

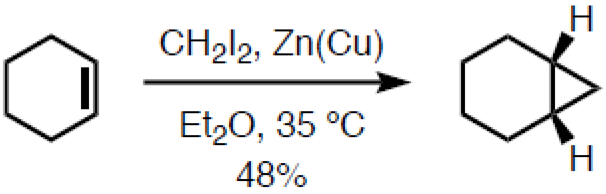


Mechanism

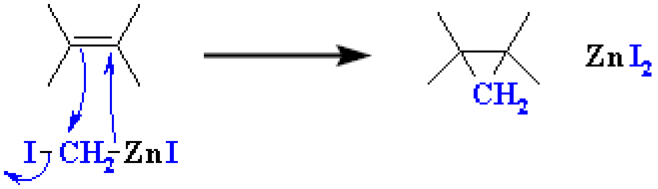


3. SIMMONS-SMITH REACTION — ZINC REAGENTS IN CYCLOPROPANATION

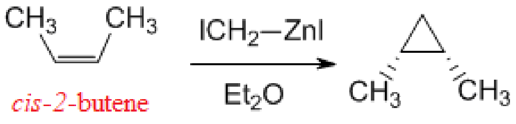
Reaction between diidomethane and a zinc-copper couple gives *reactive carbenoid intermediate Iodomethylzinc iodide (ICH_2ZnI)*

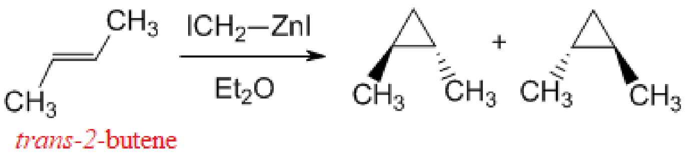


MECHANISM: Concerted reaction- Simultaneous formation of both C-C bonds .

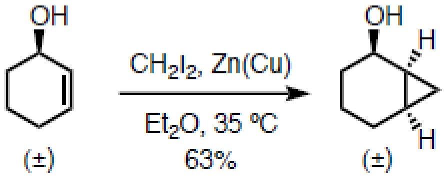


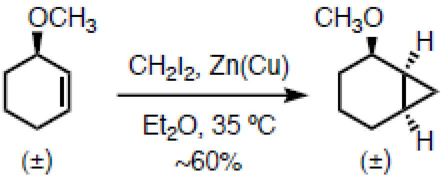
- Reaction is stereospecific with respect to the alkene





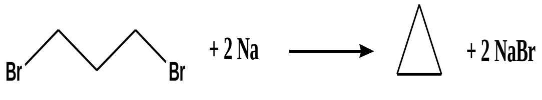
- Diastereoselective cyclopropanation is possible in the presence of directing groups:

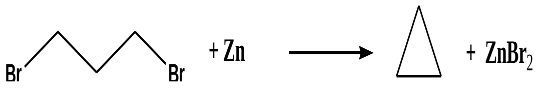




•FROM 1,3-DIBROMOPROPANE BY WRUTZ REACTION

1,3-Dibromopropane cyclizes in the presence of sodium metal under anhydrous conditions to give cyclopropane. The yield of this reaction can be improved by using zinc metal.



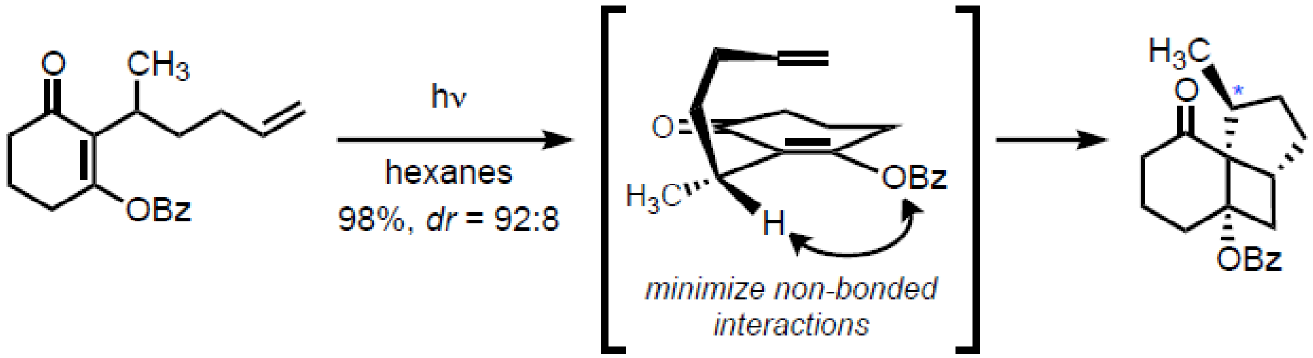


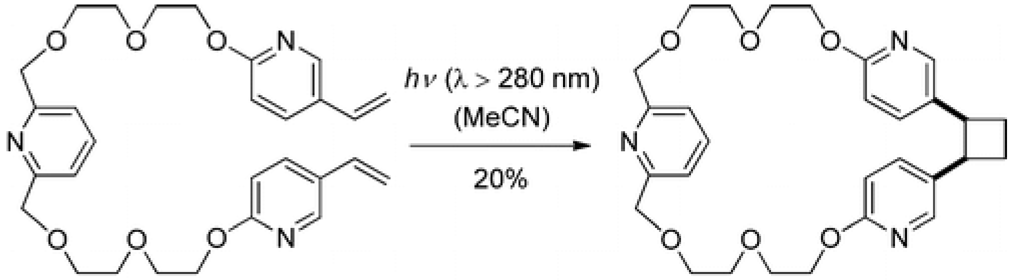
Synthetic methods for the Construction of Cyclobutanes: You have studied conventional methods like 1,3-dibromopropane with malonic acid diethyl ester in the presence of a base etc. at UG level so we will not discuss those methods.

BY [2+2] CYCLOADDITIONS: Suprafacial [2+2] cycloadditions are *photochemically allowed* but thermally forbidden.

•Intramolecular [2+2] Cycloadditions

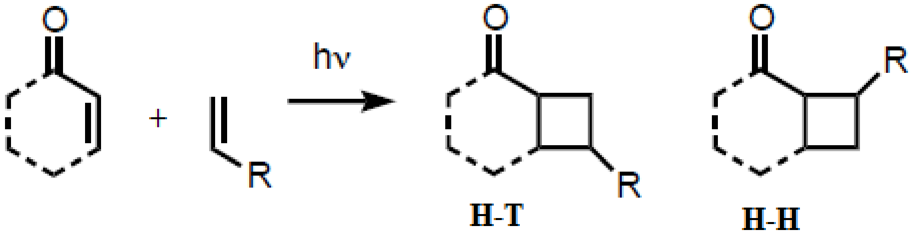
Intramolecular [2+2] cycloadducts are readily formed. Tethers are generally 2 to 4 atoms long:



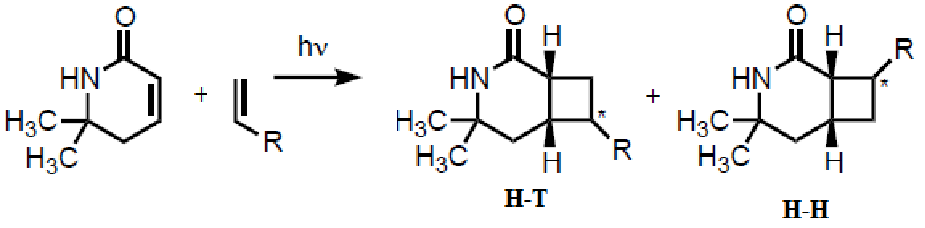


Inokuma, S.; Yatsuzuka, T.; Ohtsuki, S.; Hino, S.; Nishimura, J. Synthesis of Crownophanes Possessing Three Pyridine Rings Tetrahedron **2007**, 63, 5088– 5094

- **Intermolecular [2+2] Cycloadditions**



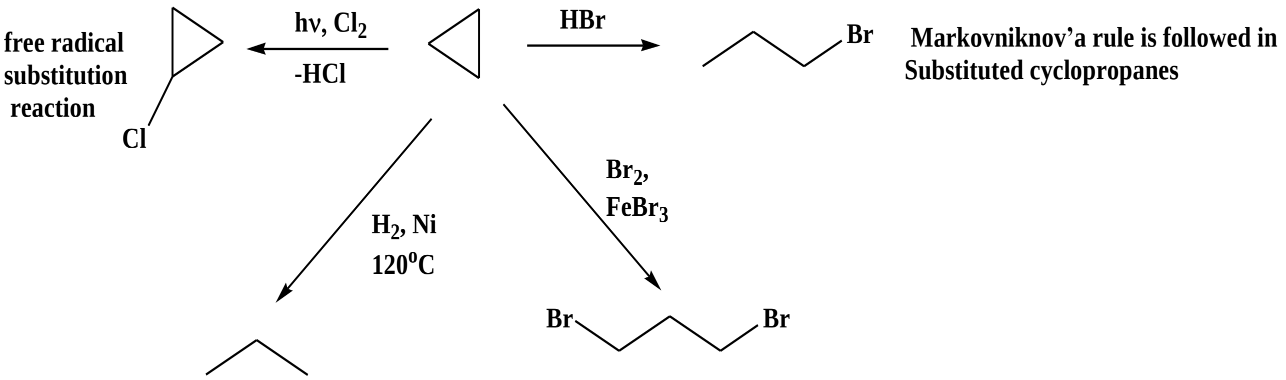
Regioselectivity: In general, H-T isomer is favored when R is electron donating and H-H isomer is favored when R is electron withdrawing



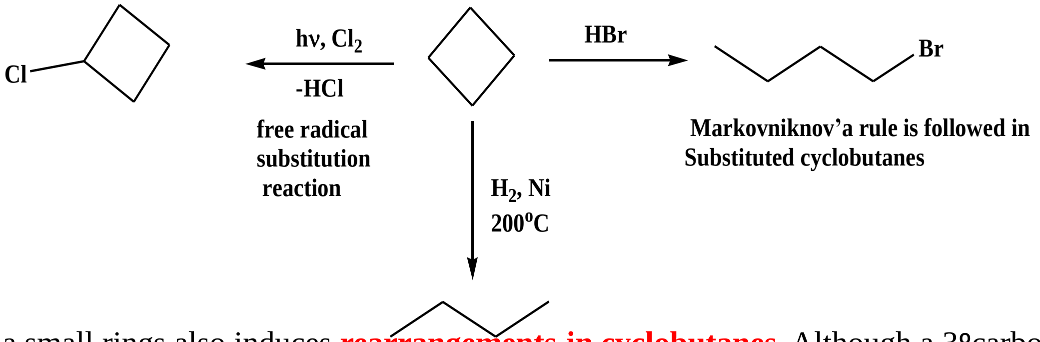
R	*d.r.* (HT : HH)
CN	18 : 82
OEt	95 : 5

Reactions of cyclopropane and Cyclobutanes

The cyclopropane ring undergoes ring substitution reactions such as **Halogenation,** and ring opening reactions such as **Addition reactions (Hydrohalogenation, bromination, hydrogenation, hydration etc.)**.

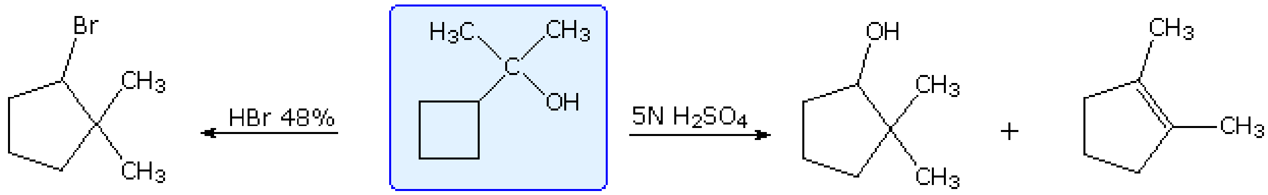


The cyclobutane ring undergoes ring substitution reactions such as **Halogenation,** ring opening reactions such as **Addition reactions (Hydrohalogenation, bromination, hydrogenation, hydration etc.)** and ring expansion reactions.



- Strain in a small rings also induces **rearrangements in cyclobutanes**. Although a 3ºcarbocation is initially formed, the angle and torsional strain of the four-membered ring is reduced by a methylene group shift resulting in ring expansion to a 2ºcarbocation.

Ring Expansion Rearrangement



Mechanism