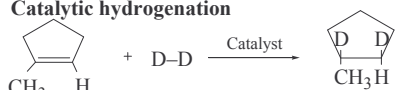


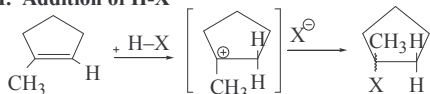
Summary of CH 12 Reactions of Alkenes

I. Catalytic hydrogenation

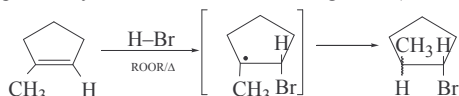


- Requires a transition metal as catalyst: Pd-C, PtO₂, Raney-Ni
- Stereospecificity: syn addition--the two atoms are added to the same face of the double bond.

II. Addition of H-X

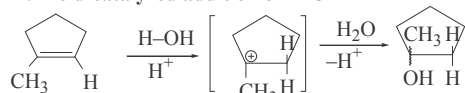


- Ionic mechanism via a C⁺ intermediate
- relative stability for C⁺: 3° > 2° > 1°
- regioselectivity: Markovnikov rule (preferring a more stable C⁺)
- stereospecificity: racemic products (X⁻ could attack from either side of the sp² C⁺ intermediate)
- possibility for carbon skeleton rearrangement (to a more stable C⁺)



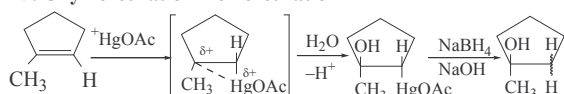
- Radical mechanism via a C[•] intermediate
- requires a radical initiator (ROOR, heat)
- relative stability for C[•]: 3° > 2° > 1°
- net reaction: Anti Markovnikov addition of H-Br to an unsymmetric C=C (complementary to the ionic addition H-Br to C=C)

III. Acid-catalyzed addition of H-OH



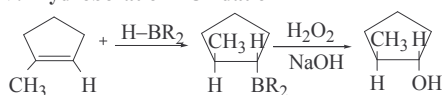
- Ionic mechanism via a C⁺ intermediate
- requires an acid as catalyst: H₂SO₄ (dil.), H₃PO₄
- regioselectivity: Markovnikov rule (preferring a more stable C⁺)
- stereospecificity: racemic products (H₂O could attack from either side of the sp² C⁺ intermediate)
- Cis/trans isomerization could be facilitated via the formation of C⁺

IV. Oxymercuration-Demercuration



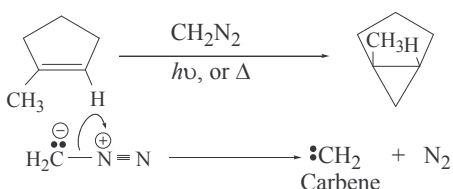
- Ionic mechanism via a Hg-bridged C⁺ for oxymercuration
- no carbon skeleton rearrangement
- regioselectivity: the Hg-bridged C⁺ from unsymmetric C=C bond is not symmetric and its opening by a nucleophile follows Markovnikov rule.
- the Hg-bridged C⁺ could be opened by nucleophiles other than H₂O, providing synthetic access to ethers (by ROH) or amines (by RNH₂)
- Radical mechanism for demercuration
- requires a reducing reagent such as NaBH₄
- stereospecificity: racemic products for C-Hg reduction
- Good alternative to the acid-catalyzed hydration if the carbon skeleton could undergo rearrangement.

V. Hydroboration - Oxidation



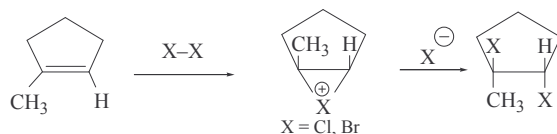
- Concerted mechanism for hydroboration
- regioselectivity: B binds to the less hindered C
- stereospecificity: syn addition of B-H to C=C
- Concerted mechanism for oxidation
- stereospecific migration of R (retention of configuration) for oxidation of R₃B by H₂O₂
- Net reaction: Anti Markovnikov addition of H-OH to an unsymmetric C=C (complementary to acid-catalyzed hydration or oxymercuration-demercuration)

VI. Addition of carbene :CH₂

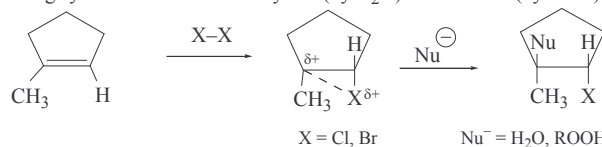


- Concerted mechanism

VII. Addition of Br₂ and Cl₂

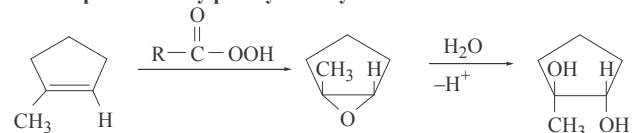


- Ionic mechanism via a halonium ion intermediate
- stereospecificity: anti addition -- the two atoms are added to the opposite face of the double bond.
- regioselectivity: halonium ion from unsymmetric C=C bond is not symmetric and its opening by a nucleophile follows Markovnikov rule
- the halonium ion intermediate could be opened by Nu⁻ other than X⁻, providing synthetic access to halohydrin (by H₂O) or haloether (by ROH).



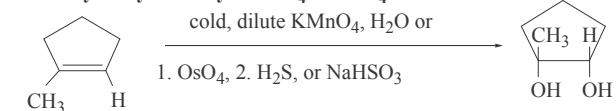
- halohydrins as precursor for epoxide provides an alternative for epoxide synthesis by alkene epoxidation

VIII. Epoxidation by peroxycarboxylic acid



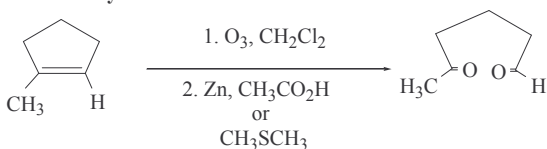
- Stereospecificity for epoxidation: syn addition of O to C=C via a concerted mechanism
- Stereospecificity for H⁺ catalyzed ring opening of oxirane by H₂O: anti-1,2-diol, making anti-1,2-diol from alkene in two steps, complementary to the syn dihydroxylation of alkene by KMnO₄ or OsO₄

IX. Dihydroxylation by KMnO₄ or OsO₄



- Stereospecificity: syn dihydroxylation via a concerted mechanism
- The osmate intermediate from OsO₄ oxidation is stable enough and undergoes reductive hydrolysis, requiring a reducing agent such as H₂S or NaHSO₃
- Complementary to the anti dihydroxylation by epoxidation-hydrolysis reactions

X. Ozonolysis



- Reductive decomposition of the ozonide (with Zn/CH₃CO₂H or CH₃SCH₃) yields ketone or aldehyde
- Disubstituted C of the C=C gives ketone, monosubstituted C of the C=C gives aldehyde, and the terminal C of C=CH₂ gives formaldehyde

XI. Test of alkenes

- Decolorization of Br₂/CCl₄ (brown)
- Decolorization of KMnO₄/H₂O (purple)