Epoxides - Formation and ring opening

By
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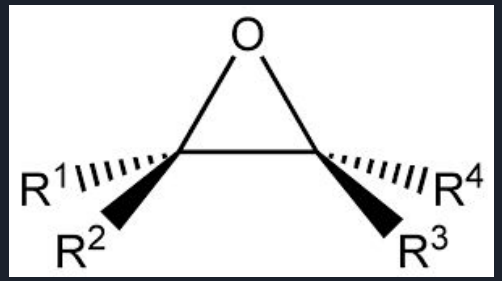
Learning Outcomes

- Define epoxide
- Understand the structure of epoxides
- Mechanism behind the formation of epoxides
- Write Cleavage of ring

Introduction

- An epoxide is a cyclic ether with three-atom ring.
- The shape is triangle.
- It is a strained ring, hence highly reactive than other ethers
- They produced on large scale for many applications

General structure



- Used as Fumigant and Antifreeze.

Preparation

Epoxidation of alkenes (Prilezhaev reaction)

Alkene ⟶ epoxi group (epoxidation)

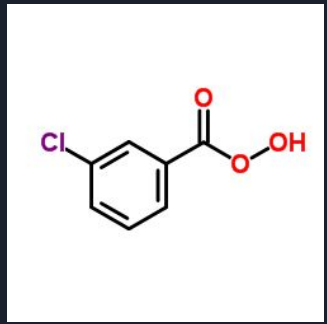
Oxidation reagent (which can donate a ‘O’) where an extra oxygen is present

i.e. Peroxides (-- O -- O --) consists a weak bond

Eg : CH_3COOOH or CH_3CO_3H - peracetic acid (PAA)

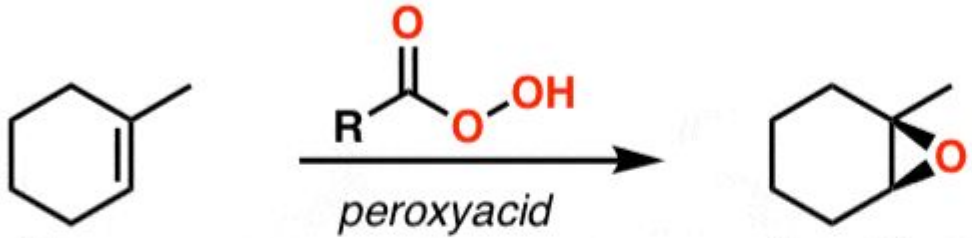
$PhCOOOH$ or $PhCO_3H$ - perbenzoic acid (PBA)

Common reagent is MCPBA (meta chloro perbenzoic acid)



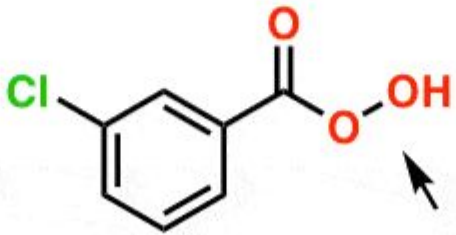
Epoxide synthesis (1):

Epoxides can be made from alkenes with a peroxyacid [RCO_3H]



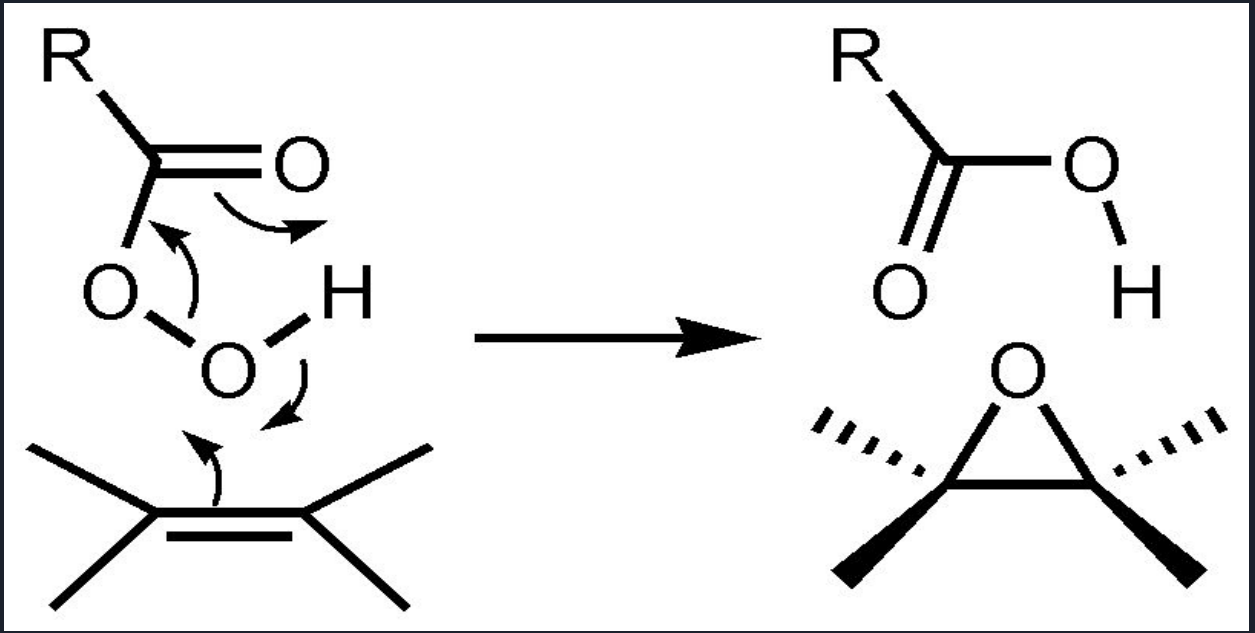
A very popular peroxyacid: *m*-CPBA

[*m*-chloroperoxybenzoic acid]



*note the **two** oxygens here - the weak O–O bond gives peroxyacids their reactivity*

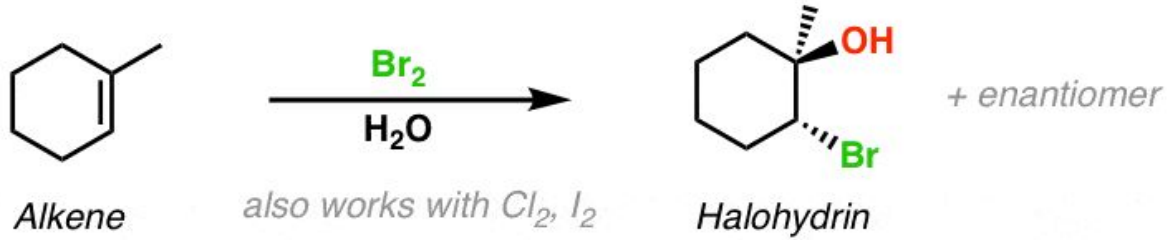
Mechanism



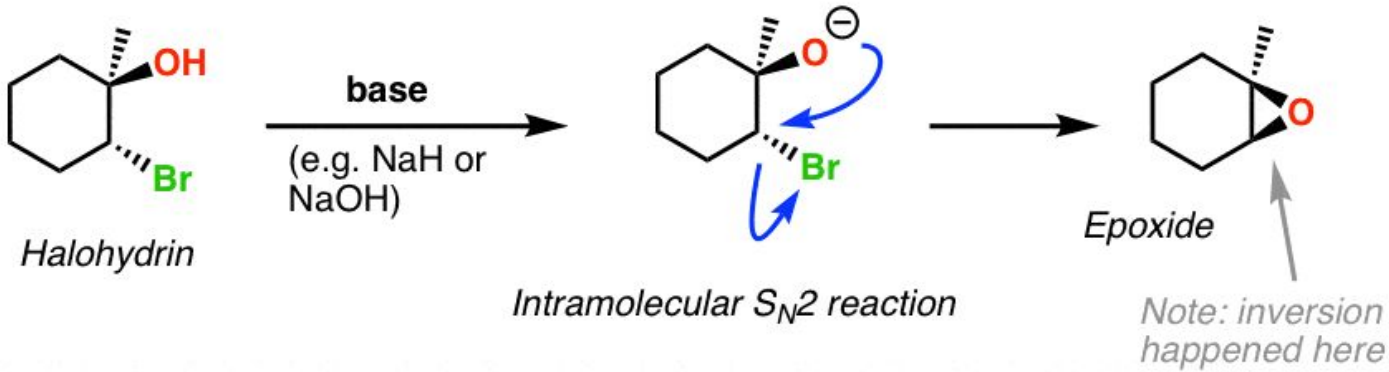
Epoxide synthesis (2):

Epoxides can also be made through treating halohydrins with base

Recall how we make halohydrins from alkenes:

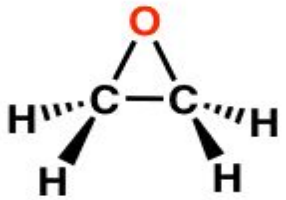


Adding base leads to an intramolecular S_N2 reaction, forming the epoxide



Epoxide ring opening

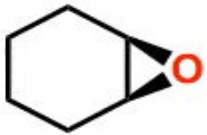
Epoxides ["oxiranes"] are an unusually reactive type of cyclic ether



"ethylene oxide"

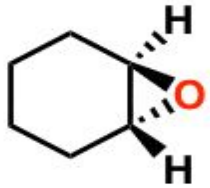
Epoxide

- Interior bond angles of 60° (compare to ideal angle of 109°)
- Destabilized by **ring strain** [about 13 kcal/mol]
- When attached to a ring, both C–O bonds are *cis*



OK

"cis" ring junction

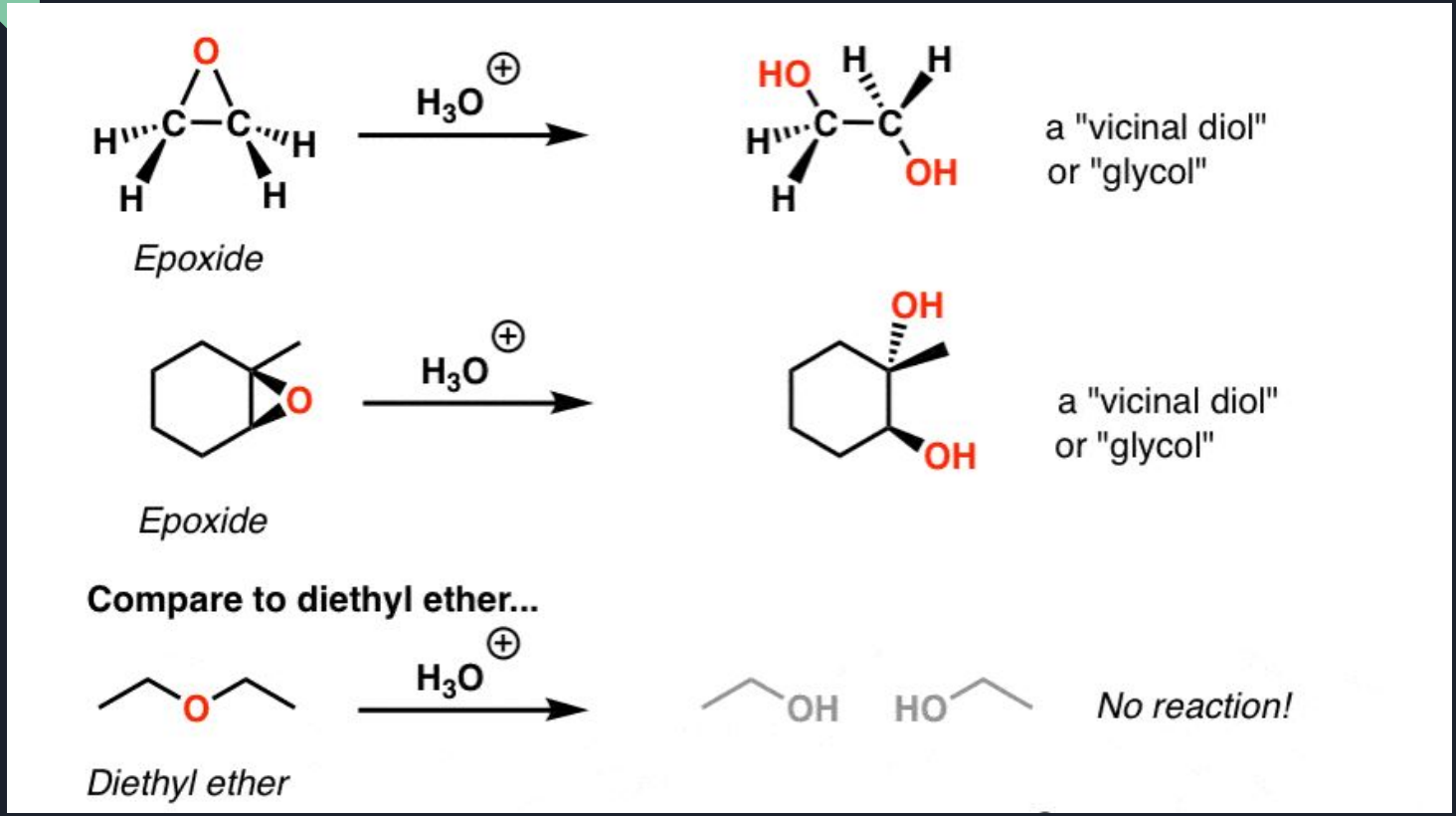


Does not exist (too strained!)

"trans" ring junction

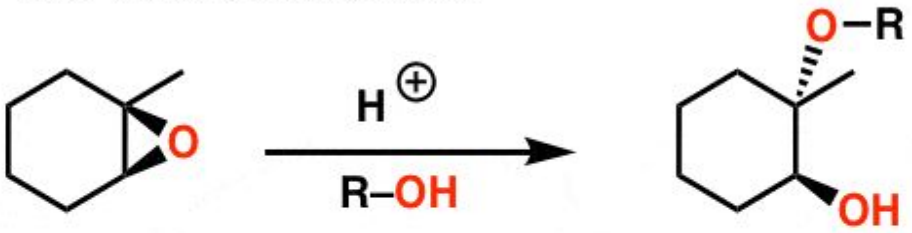
By Acid

Epoxides react with Aqueous acids under mild conditions to form diols

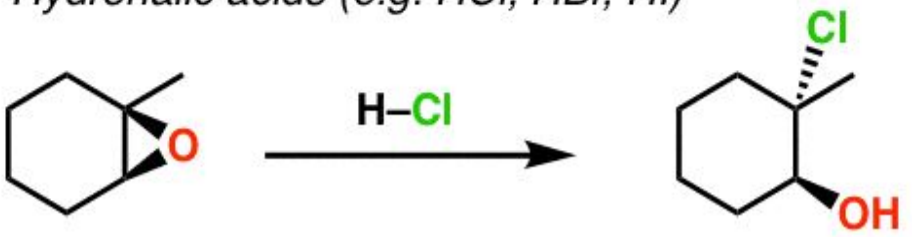


Other nucleophiles (besides water) can be used

With alcohols as solvent:



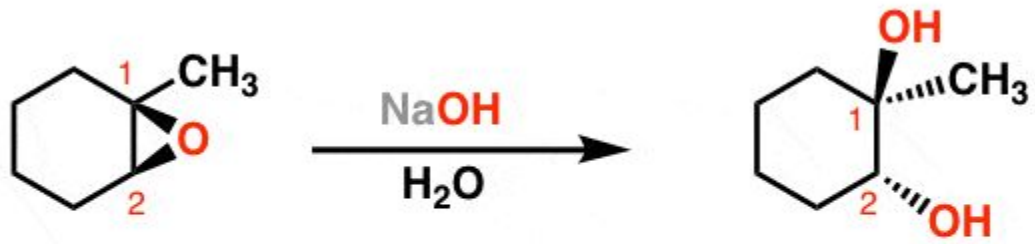
Hydrohalic acids (e.g. HCl, HBr, HI)



Attack still occurs
on the most subst
carbon of the epo

By base

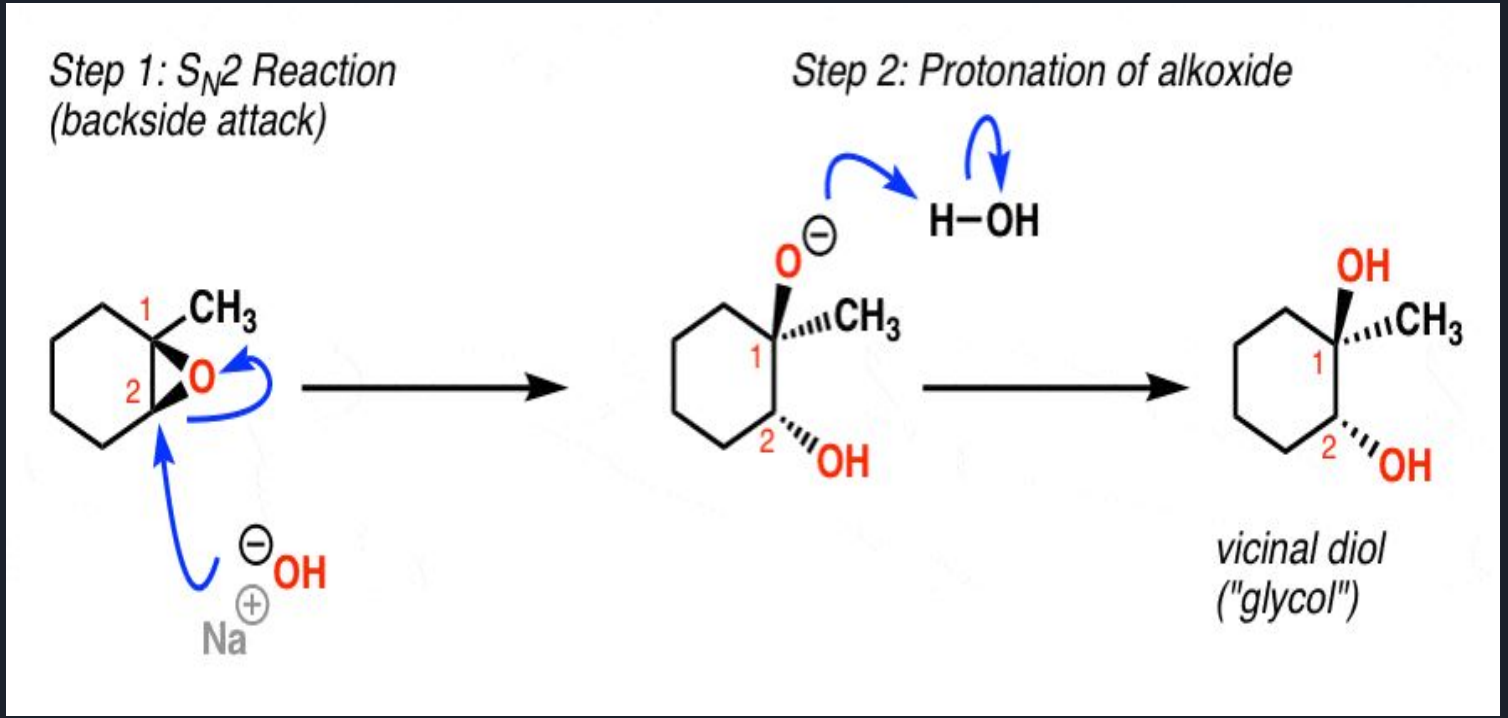
Reactions of Epoxides Under Basic Conditions Proceed Via an S_N2 Reaction



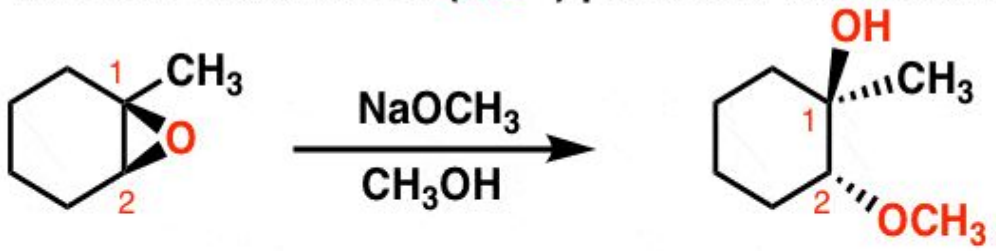
- *Attack of nucleophile at least substituted position*
- *Note that stereochemistry at C-2 is inverted*

Can also use $RO^{\ominus}$, Grignard reagents, organolithium reagents, $LiAlH_4$

Mechanism


Step 1: S_N2 Reaction
(backside attack)
Step 2: Protonation of alkoxide
1
CH3
2
O
OH
Na
H–OH
O
CH3
1
2
OH
OH
CH3
1
2
OH
vicinal diol
("glycol")

Addition of alkoxides ($RO^{\ominus}$) proceeds via the same 2-step process



Exact same mechanism as with NaOH


THANK
YOU