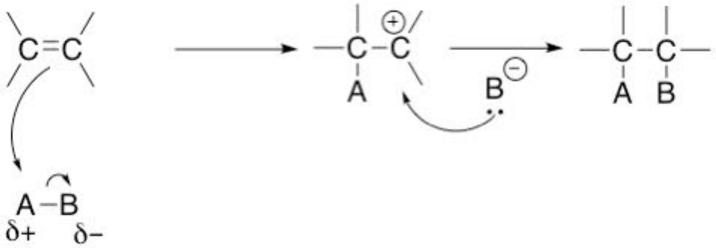
CHEM 261 March 16, 2023

Recall:

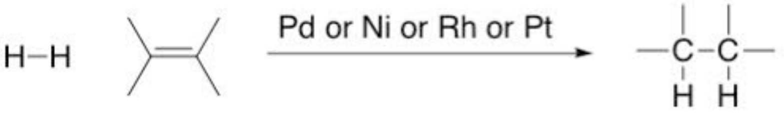
Addition Reactions

- Occurs on double bonds and triple bonds



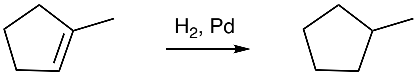
Hydrogenation

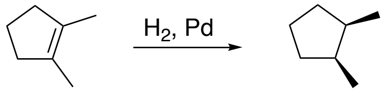
Example 1:



- cis or syn addn
- stereospecific

Example 2:

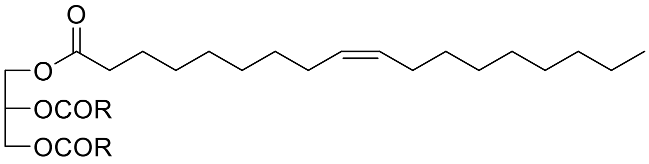




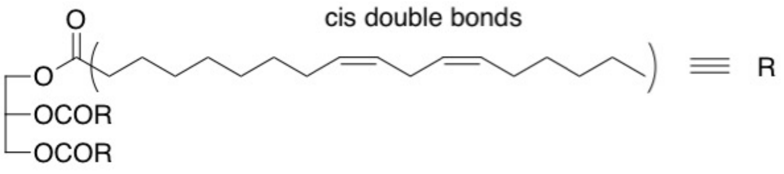
Meso compound

Example 3: Fats

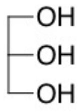
Fat



Monounsaturated triglyceride

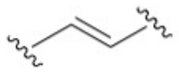


A triglyceride

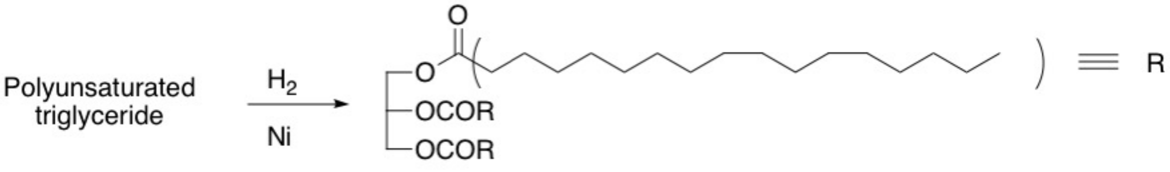


Glycerol

trans double bond



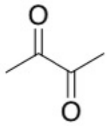
- The triglyceride is a triester of glycerol
- It is a polyunsaturated (>1 double bond) fats (e.g. canola oil)- unsaturation refers to the double bonds.
- Trans double bonds can also be generated in fats, which are then called trans fats.
- Hydrogenation give saturated fats (**unsaturation removed**)



Major component of margerine

A solid saturated fat (margarine)

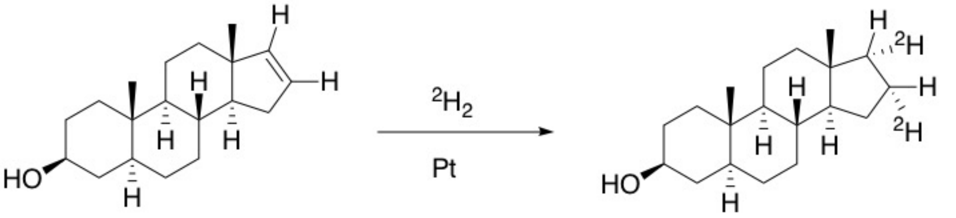
This molecule has greater London dispersion forces, cause it to exist as a solid



Diacetyl

Butter flavoring that adds a yellow color

Example 4: Steroid

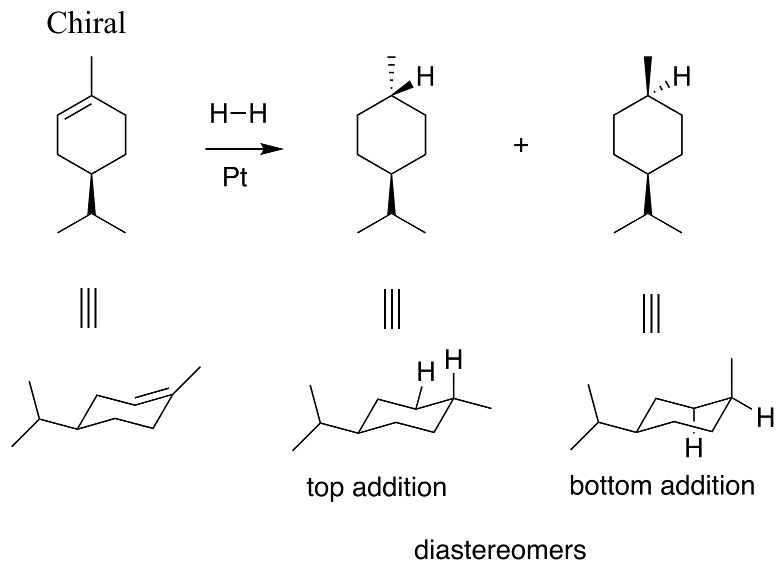


The deuteriums add to the back because of the steric hindrance of the nearby methyl group.

$^{2}H = D =$ deuterium

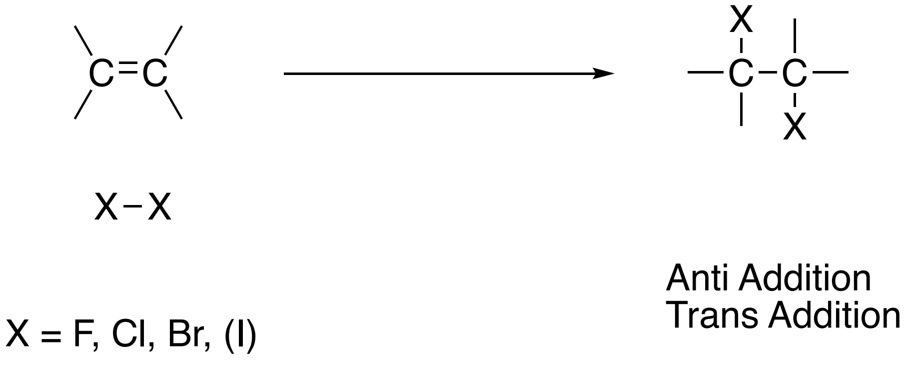
Example 5: Limonene

Limonene



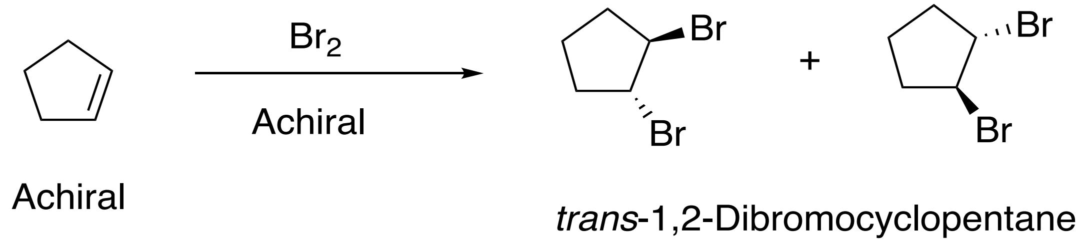
The two possible products are diastereomers and are achiral (plane of symmetry).

<u>Halogenation:</u> Addition of halogens across a double bond



Note: Iodine (I_2) does not react with most alkenes (i.e., won't add across the double bond).

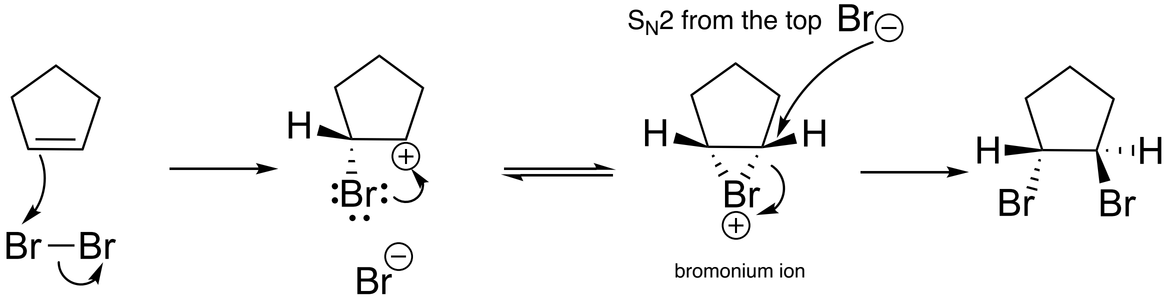
Example 1: Cyclopentene



trans-1,2-Dibromocyclopentane

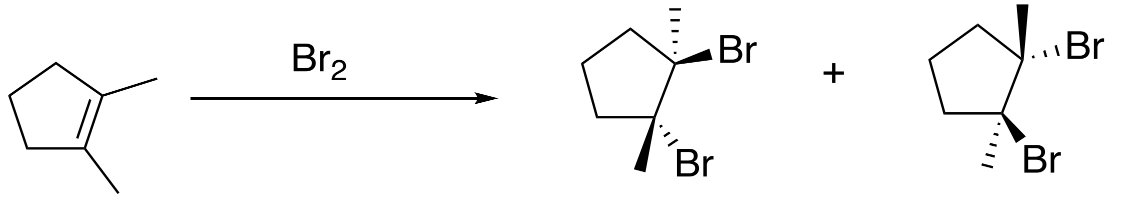
Both enantiomers formed (1:1 racemate)

Mechanism:



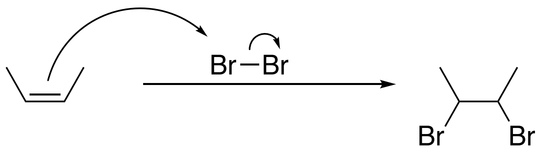
The first step can happen from the top or bottom, and the S_N2 step happens from the opposite side each time.

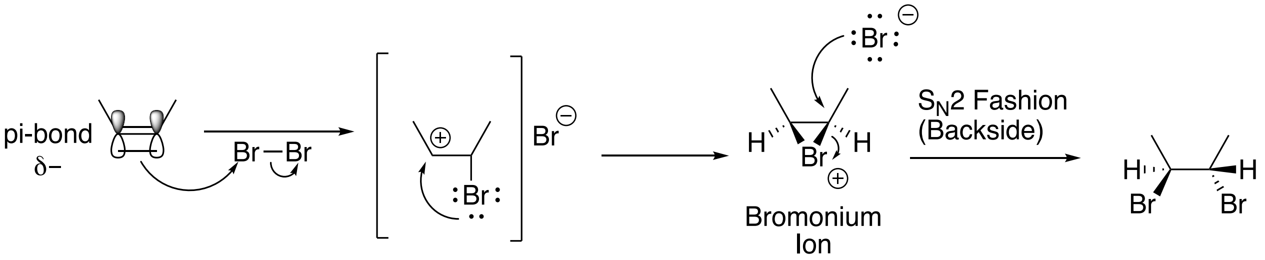
Example 2: 1,2-dimethylcyclopentene



trans-1,2-Dibromo-1,2-dimethylcyclopentane

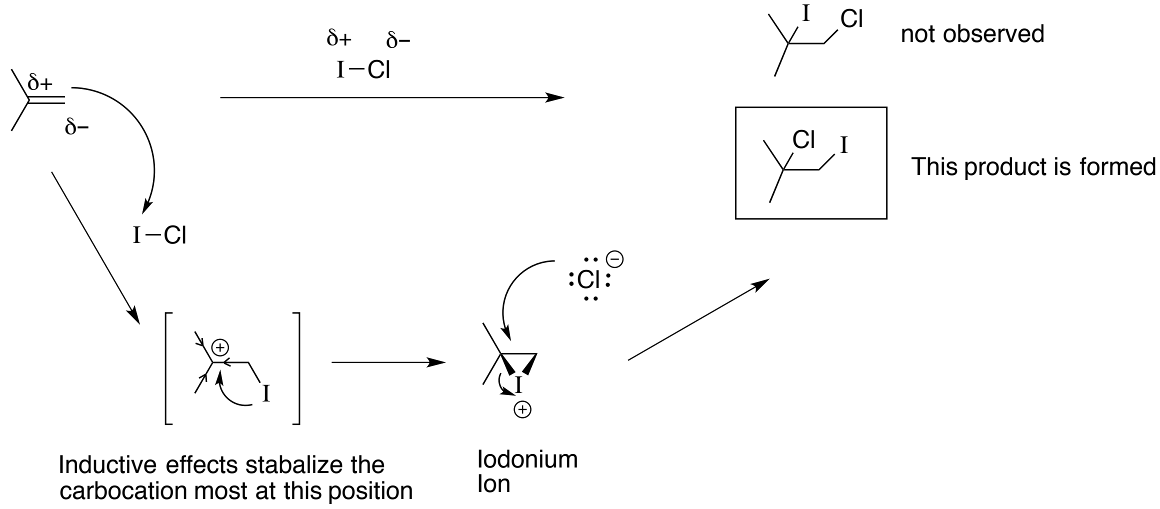
Mechanism:





- Halogen addition to alkene is very fast at -78°C
- Attack always comes from the backside – trans product
- When the bromonium ion forms, the bond between the Br and C atom can stretch, giving more carbocation character to the C.

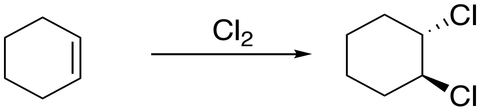
Example 3: 2-Methylpropene

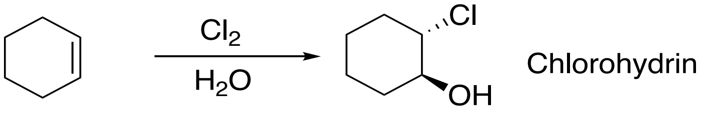


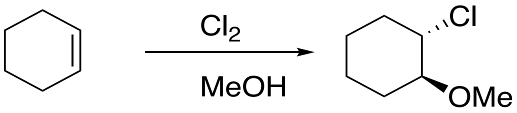
- The electrons in the π-bond attack the partially positive (δ+) I
- Cl^- will attack the more substituted C due to there being a more carbocation character (more substituted end can stabilize the positive charge better due to stabilizing effect of alkyl groups – **inductive effect**)

Markovnikov's Rule: In an addition reaction, the positive end of an A–B system (e.g. I–Cl) adds to the least substituted end of the double bond to make the more stable carbocation.

Example 4: Cyclohexene



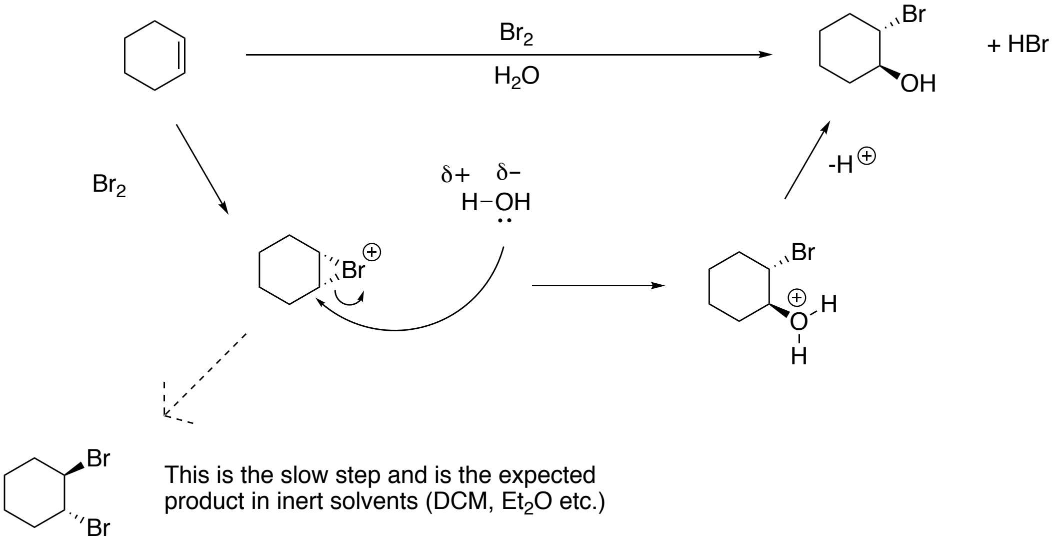




- In the presence of high concentration of H_2O (55.5 M), H_2O competes with the halide (X^-) as a nucleophile and reacts with the bromonium intermediate to form **halohydrin** – 1,2-halo alcohols.
- The same is true when using alcohols (ROH) as solvents instead of water.

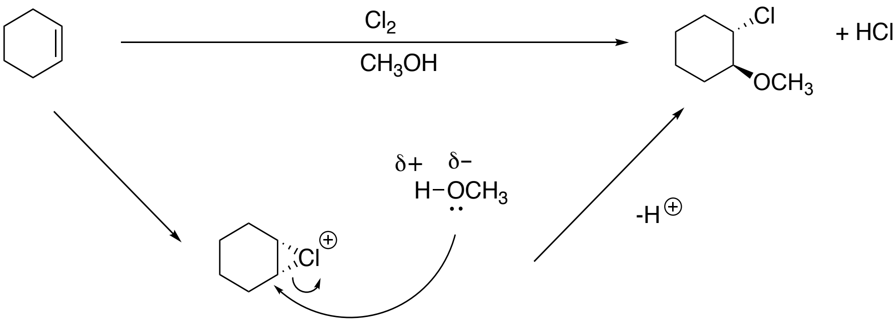
Mechanisms:

#1) Addition of an alcohol functional group (in H_2O)

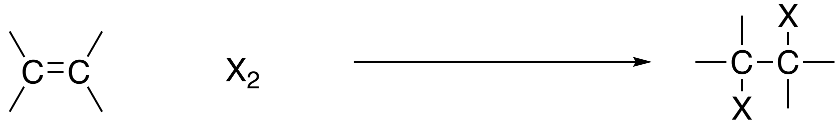


This is the slow step and is the expected product in inert solvents (DCM, Et_2O etc.)

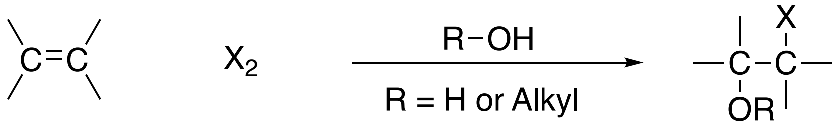
#2) Addition of an ether functional group (in CH_3OH - methanol)



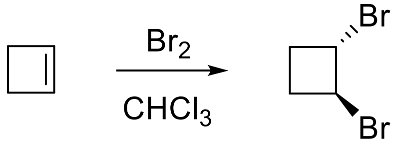
Summary:

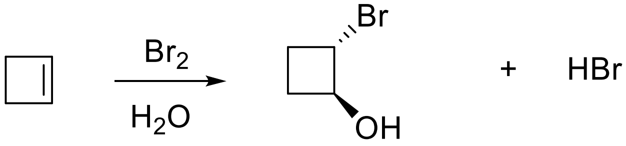


Will add in Markovnikov fashion

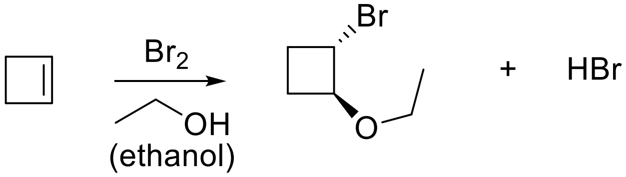


Example 5: Cyclobutene

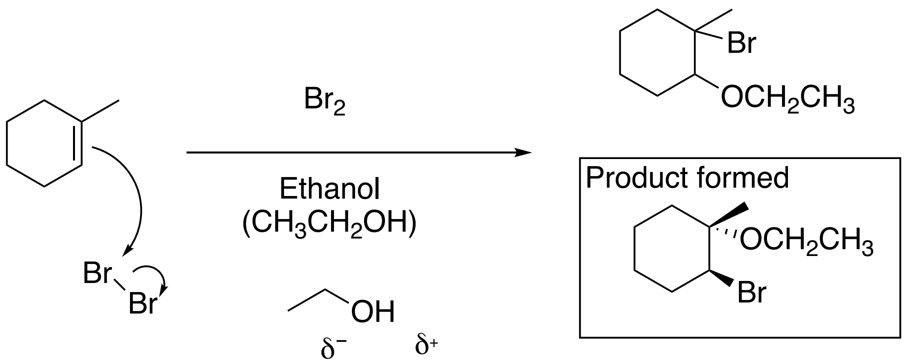




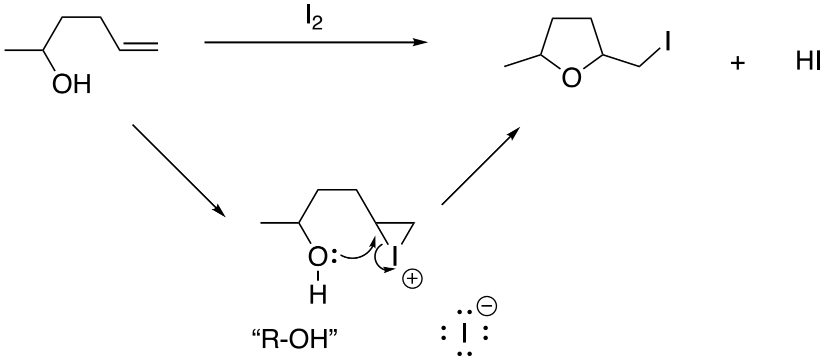
bromohydrin



Example 6: 1-methylcyclohex-1-ene

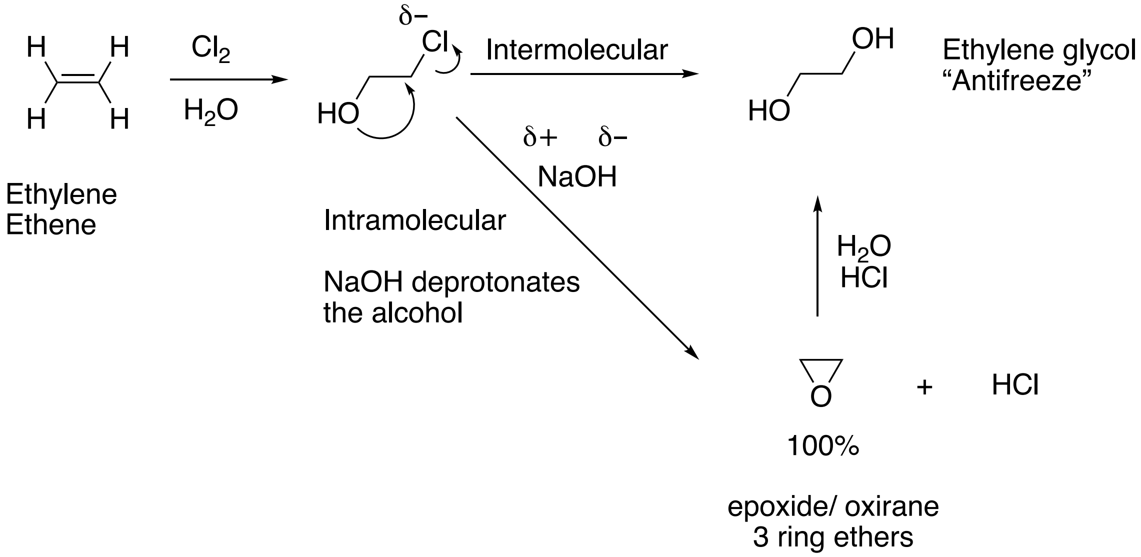


Example 7: Intramolecular



- Although iodine cannot form diiodide (I_2 cannot add to double bonds), it can form the iodinium ion.
- In the above example, the intramolecular reaction (meaning within the same molecule) occurs much much <u>FASTER</u> than the intermolecular reaction (between two or more molecules). This means that the –OH group will attack the iodonium ion much faster than the I^- group because it is an intramolecular reaction.
- Intramolecular reaction almost always beats intermolecular reactions.
- 5-membered rings form much faster than 6-membered rings.

Example 8: Ethylene (intramolecular)



- NaOH – good nucleophile and can attack a primary alkyl halide (intermolecular)
- NaOH – can act as a base and deprotonate the -OH group. The deprotonated -OH group would then attack the primary alkyl chloride to form an ethylene oxide via an Sn2 reaction (**intramolecular reaction** – within one molecule)
- Intramolecular reaction is faster than intermolecular reactions
- OH bonds break fairly easily so proton transfer reactions happen at a faster rate