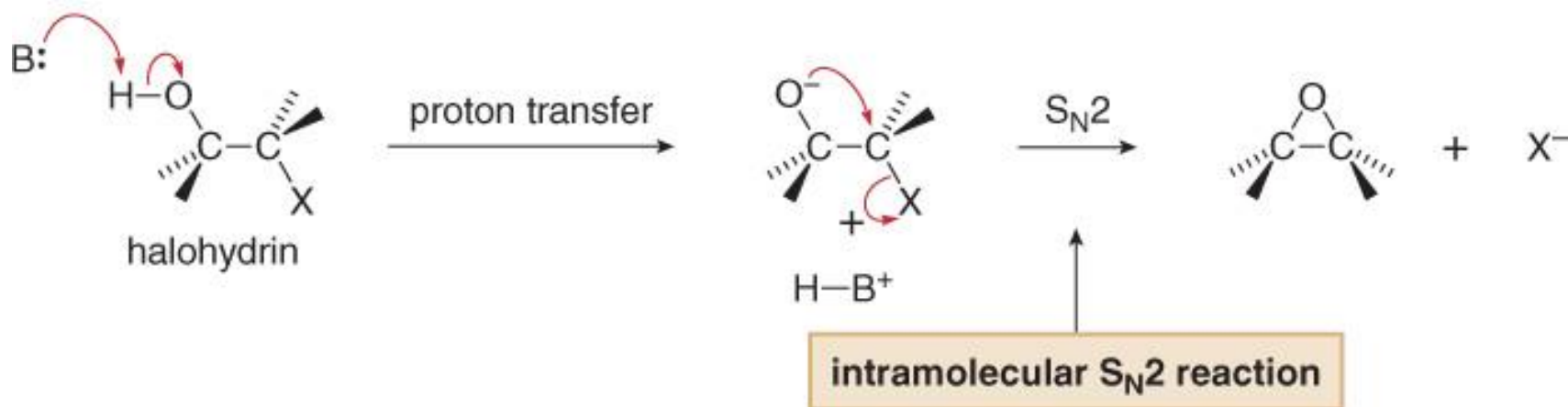


- Organic compounds that contain both a hydroxy group and a halogen atom on adjacent carbons are called **halohydrins**.
- In halohydrins, an intramolecular version of the Williamson ether synthesis can occur to form epoxides.

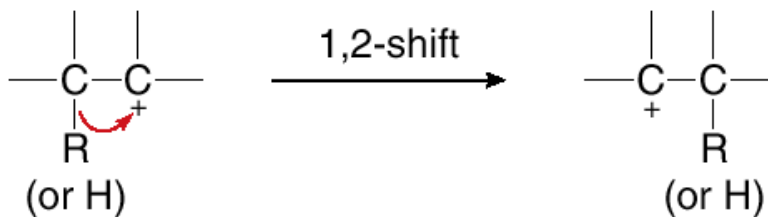
Epoxide synthesis—A two-step procedure



Carbocation Rearrangements

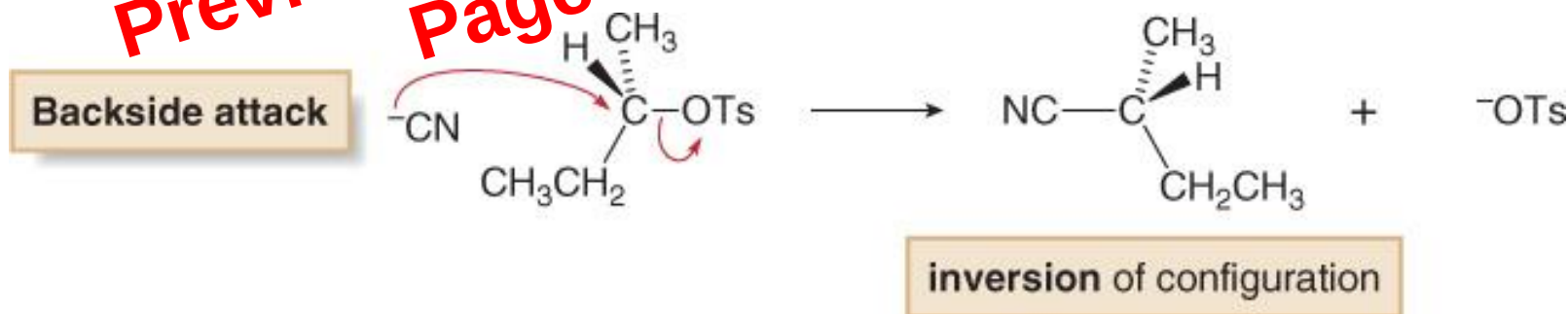
- Often, when carbocations are intermediates, a less stable carbocation will be converted into a more stable carbocation by a shift of a hydrogen or an alkyl group. This is called a **rearrangement**.
- Because the migrating group in a **1,2-shift** moves with two bonding electrons, the carbon it leaves behind now has only three bonds (six electrons), giving it a net positive (+) charge.

Carbocation
rearrangement



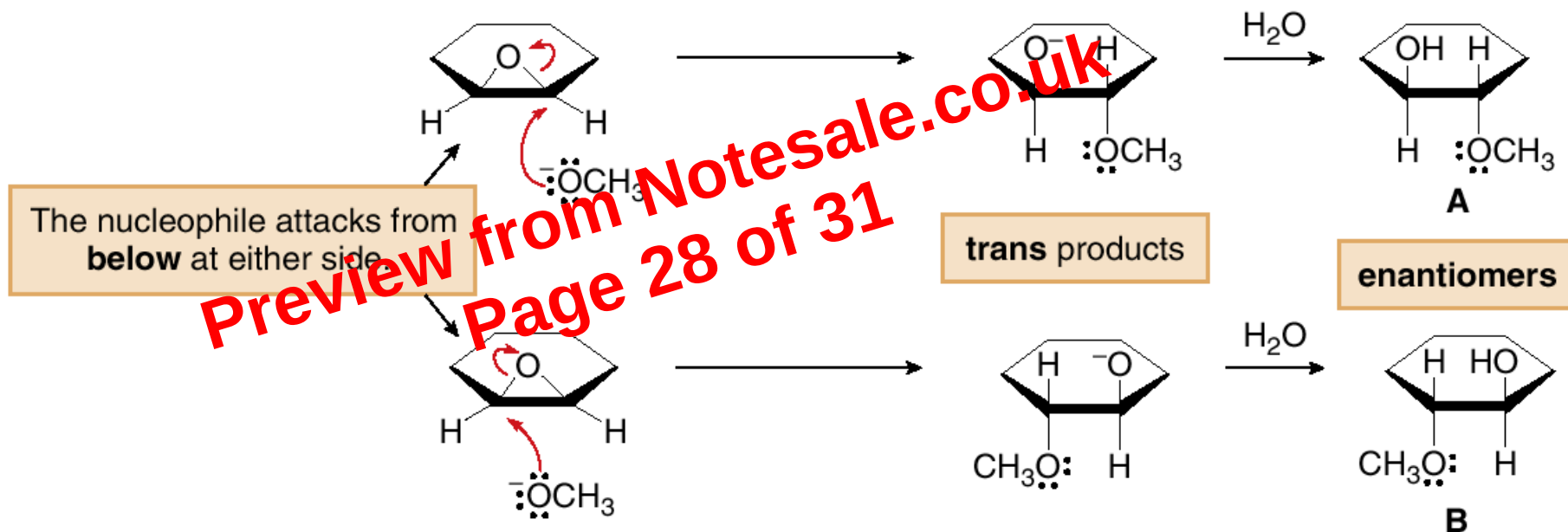
- Movement of a hydrogen atom is called a 1,2-hydride shift.
- Movement of an alkyl group is called a 1,2-alkyl shift.

- Because substitution occurs via an S_N2 mechanism, inversion of configuration results when the leaving group is bonded to a stereogenic center.



- We now have another two-step method to convert an alcohol to a substitution product: reaction of an alcohol with TsCl and pyridine to form a tosylate (step 1), followed by nucleophilic attack on the tosylate (step 2).

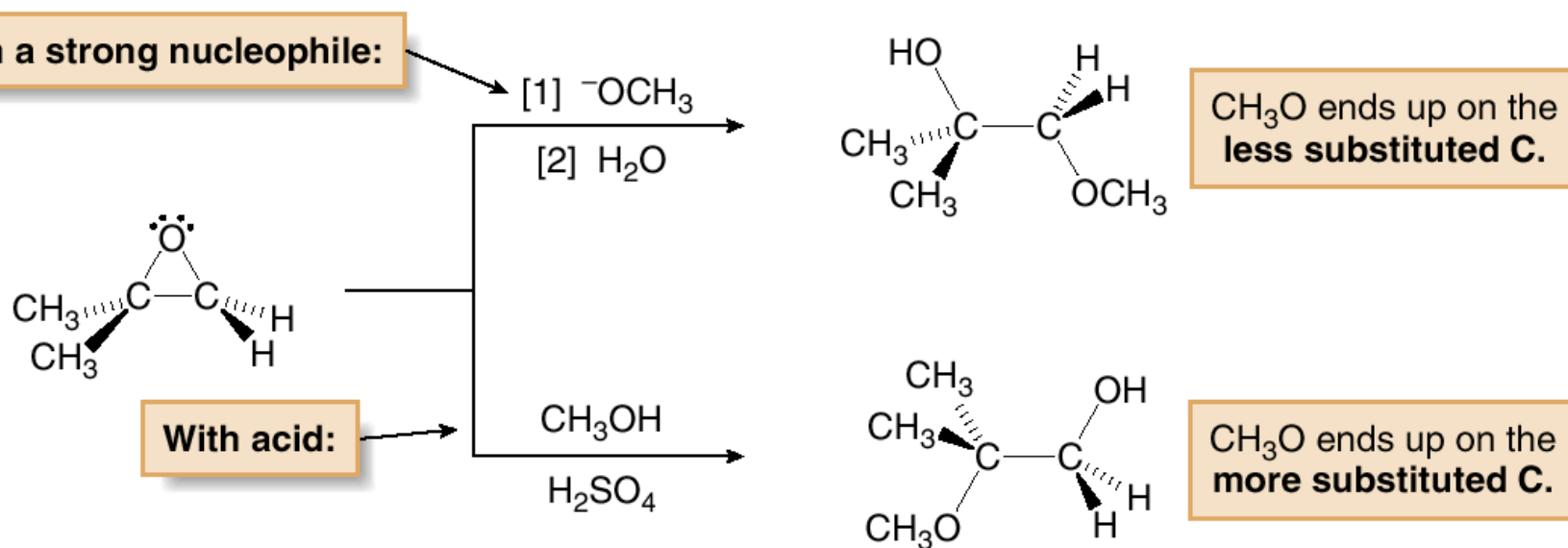




- Whenever an achiral reactant yields a product with stereogenic centers, the product must be achiral (meso) or racemic.

Optically inactive starting materials give optically inactive products!

- Ring opening of an epoxide with either a strong nucleophile or an acid HZ is regioselective because one constitutional isomer is the major or exclusive product.
- Note that the site selectivity of these two reactions is exactly opposite.



- With a strong nucleophile, $:Nu^-$ attacks at the less substituted carbon.
- With an acid HZ, the nucleophile attacks at the more substituted carbon.