



TÁMOP-4.1.1.F-14/1/KONV-2015-0006

SZTE TTIK, KTCS, 1a) Duális és moduláris
képzésfejlesztés a mesterképzéshez

Elektrofil addíció alkénekre

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020 



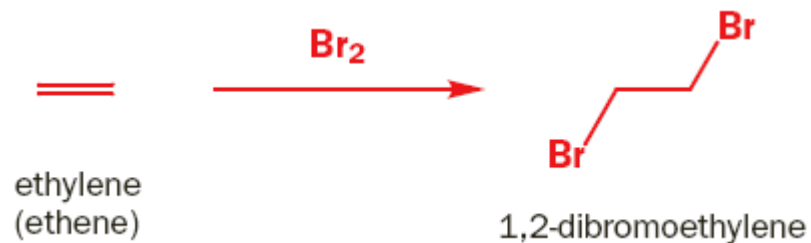
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Alap



BEFEKTETÉS A JÖVŐBE

az alapreakció



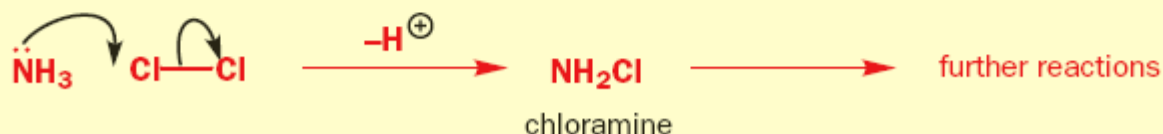
a Br_2 molekulának alacsony energiájú σ^* lazítópályája van,
így könnyen támadható nukleofilekkel

a $\text{Br}-\text{Br}$ kötés gyenge a brómatom nagy mérete miatt

Chloramines

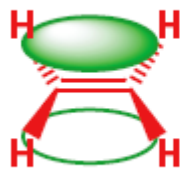
Have you ever wondered why conventional wisdom (and manufacturers' labels) warns against mixing different types of cleaning agent? The danger arises from nucleophilic attack on another halogen, chlorine. Some cleaning solutions contain chlorine (bleach, to kill moulds

and bacteria, usually for the bathroom) while others contain ammonia (to dissolve fatty deposits, usually for the kitchen). Ammonia is nucleophilic, chlorine electrophilic, and the products of their reaction are the highly toxic and explosive chloramines NH_2Cl , NHCl_2 , and NCl_3 .



mechanizmus

alkene = nucleophile



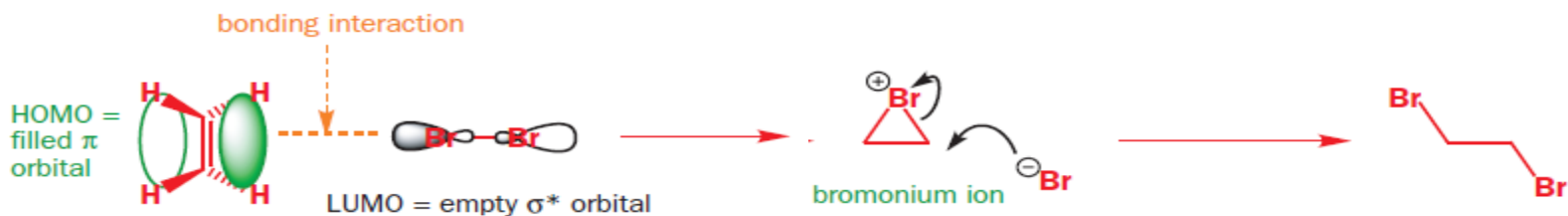
HOMO = filled π orbital

Br_2 = electrophile



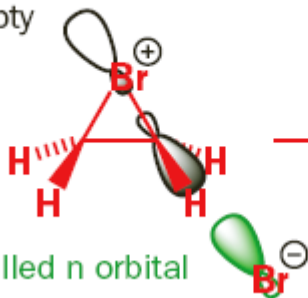
LUMO = empty σ^* orbital

electrophilic attack by Br_2 on ethylene



orbitals involved in the opening of the bromonium ion

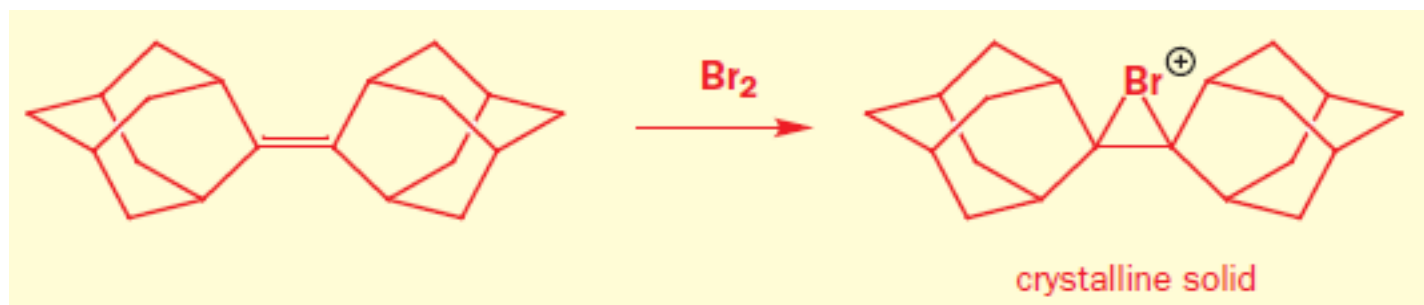
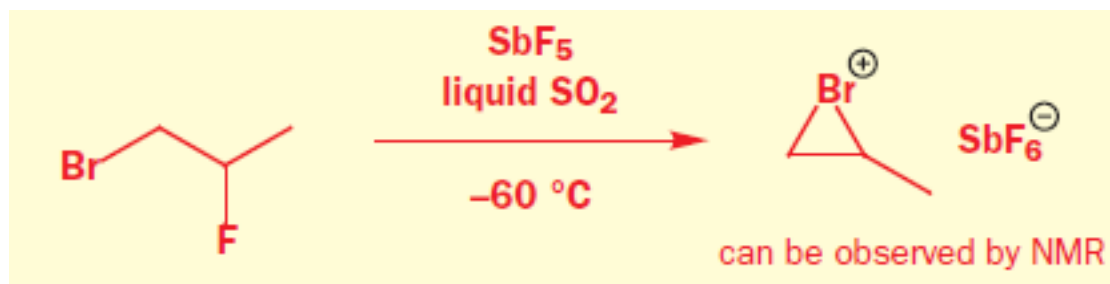
LUMO = empty σ^* orbital



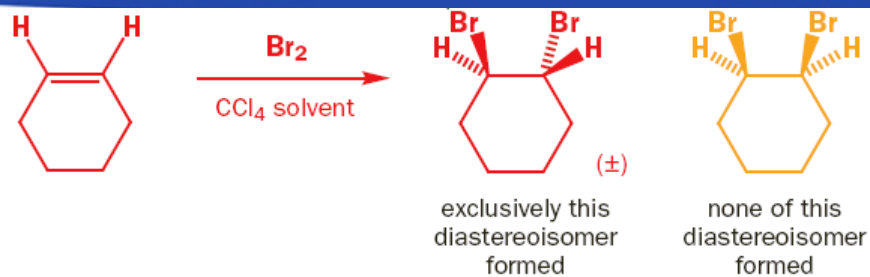
HOMO = filled n orbital

a gyűrűnyitás $\text{S}_{\text{N}}2$ mechanizmusú

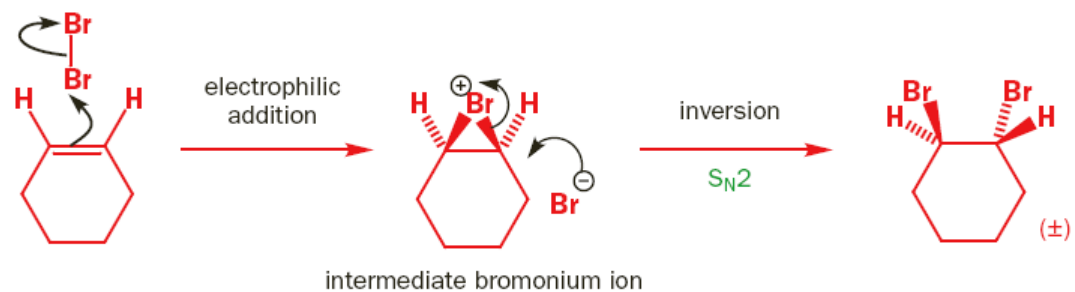
honnán tudjuk, hogy gyűrűs bromónium ion van



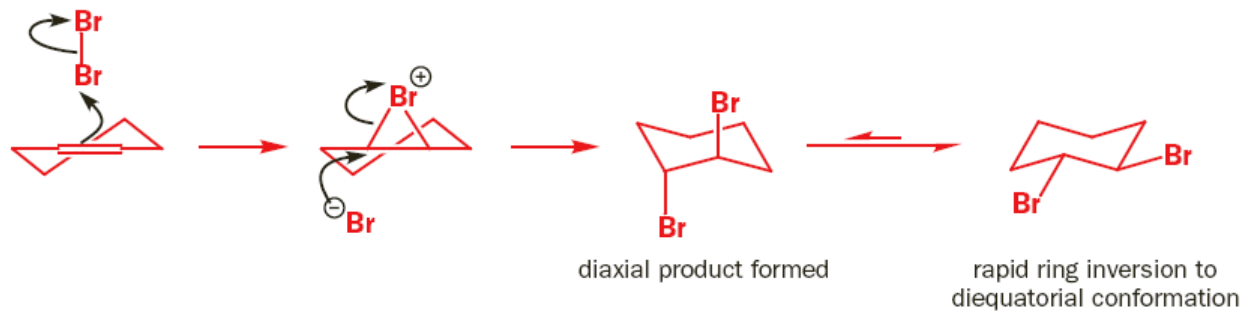
a brómaddíció *anti* addíció (sztereoizomerek képződhetnek)



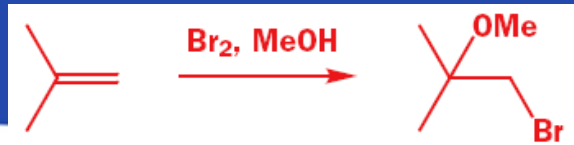
a mechanizmus



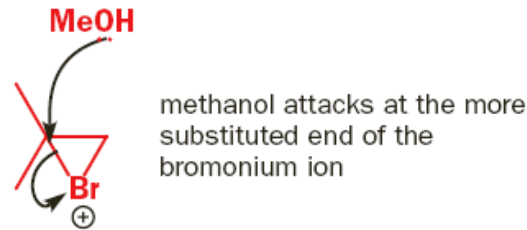
másként ábrázolva



a nem szimmetrikus bromónium ion gyűrűfelnyílása régioszelektív



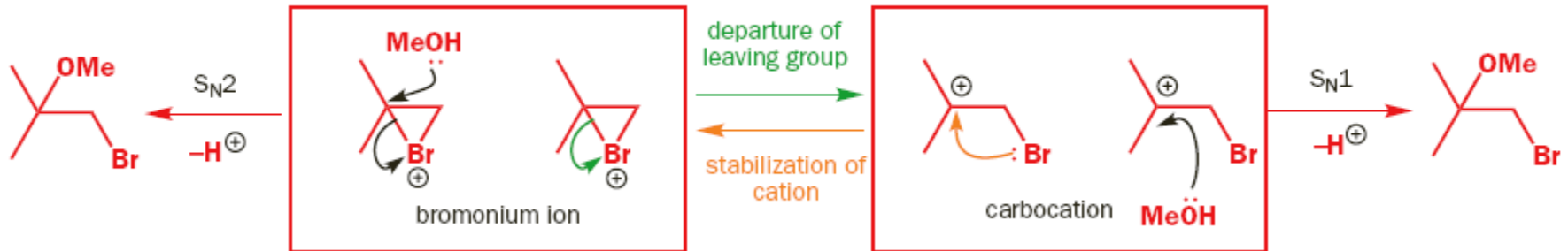
kísérleti tény



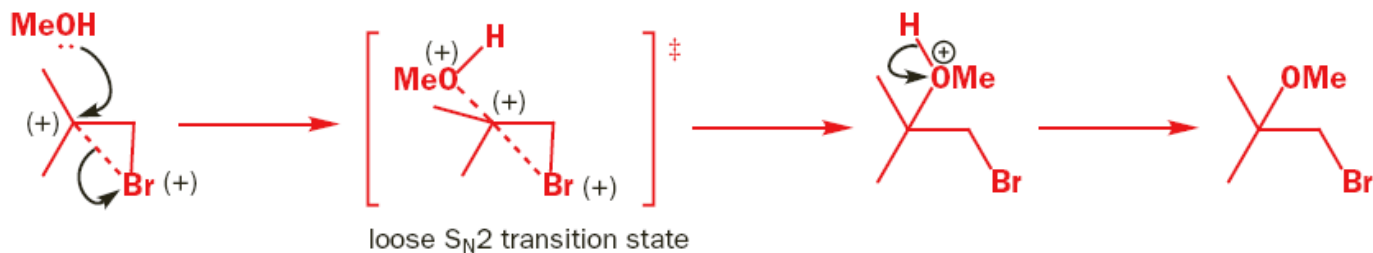
a metanol oldószer és bár nukleofilitása kisebb mint a bromid ioné, de koncentrációja sokkal nagyobb, így sikerrel versenyez

a lehetséges mechanizmusok

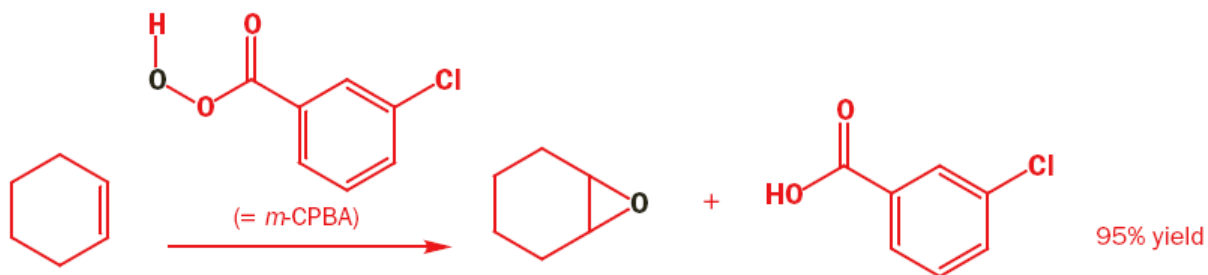
two limiting mechanisms for substitution on bromonium ion



a valószínű mechanizmus

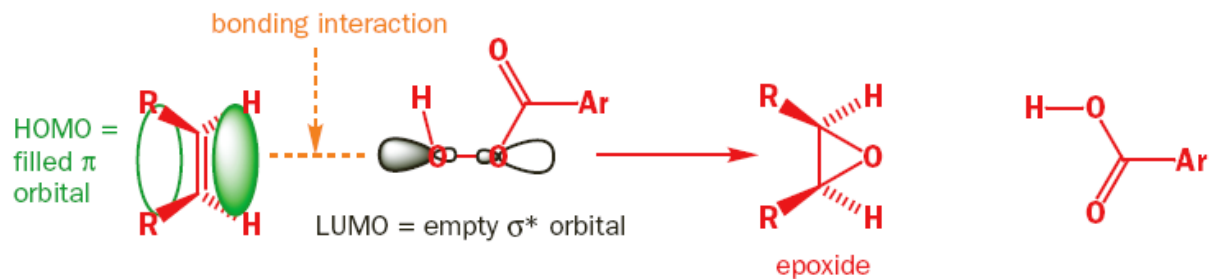


epoxidálás

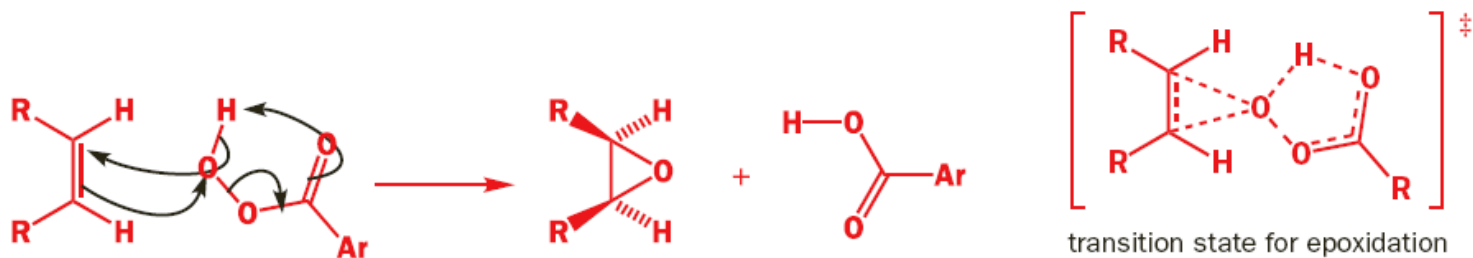


a mechanizmus

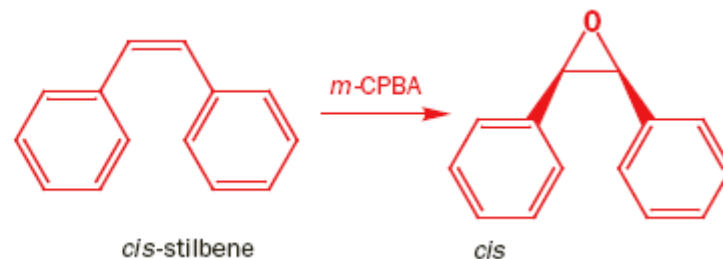
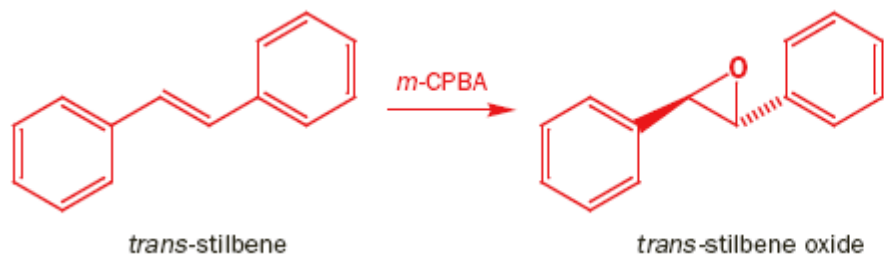
electrophilic attack by a peroxy-acid on an alkene



másként ábrázolva

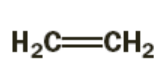
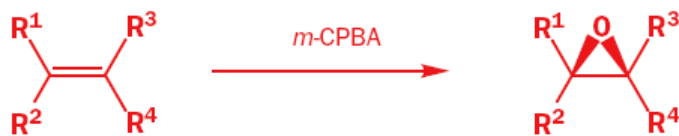


az epoxidálás sztereospecifikus



a szubsztituáltabb olefinek gyorsabban epoxidálhatók

relative rates of reaction of alkenes with *m*-CPBA



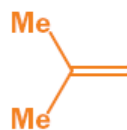
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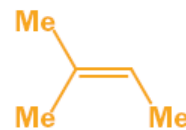
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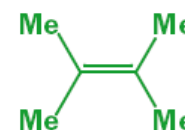
500



500

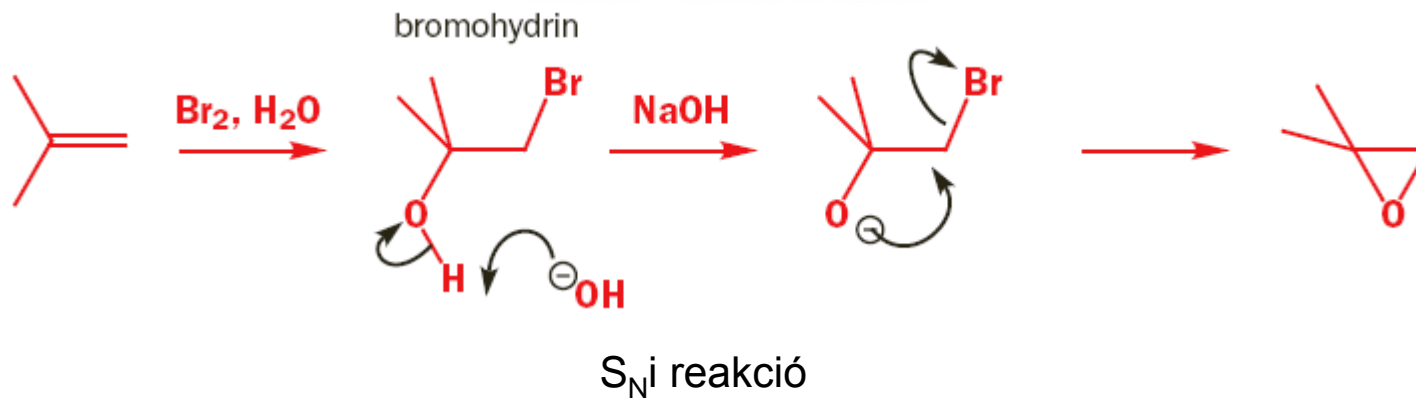


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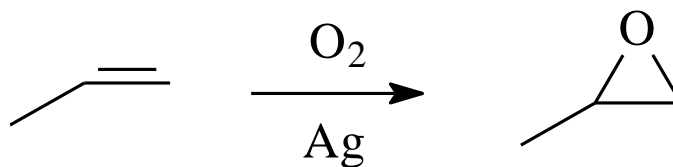


>6500

epoxidálás másként

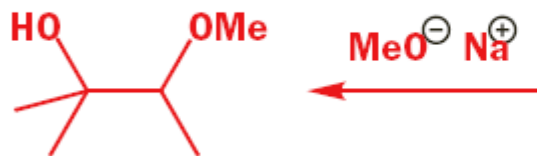


epoxidálás még másként



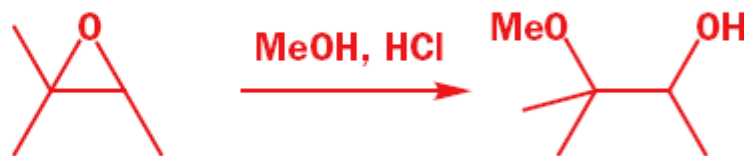
epoxidok gyűrűnyitási reakciói

reaction of epoxide with basic methoxide



attack at less substituted end

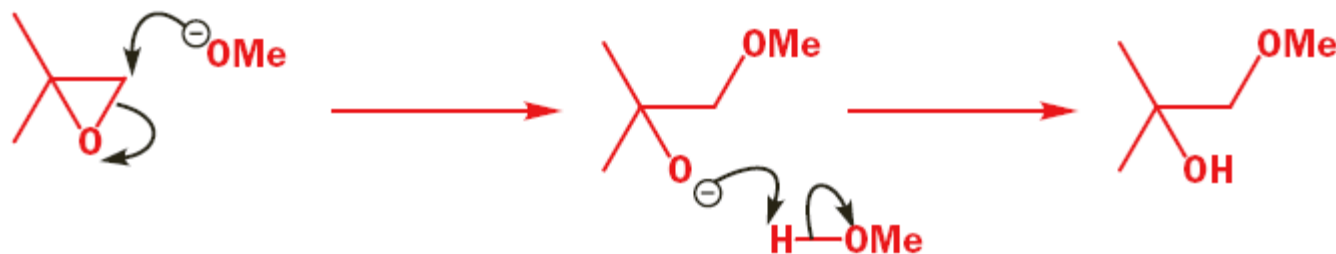
reaction of epoxide with acidic methanol



attack at more substituted end

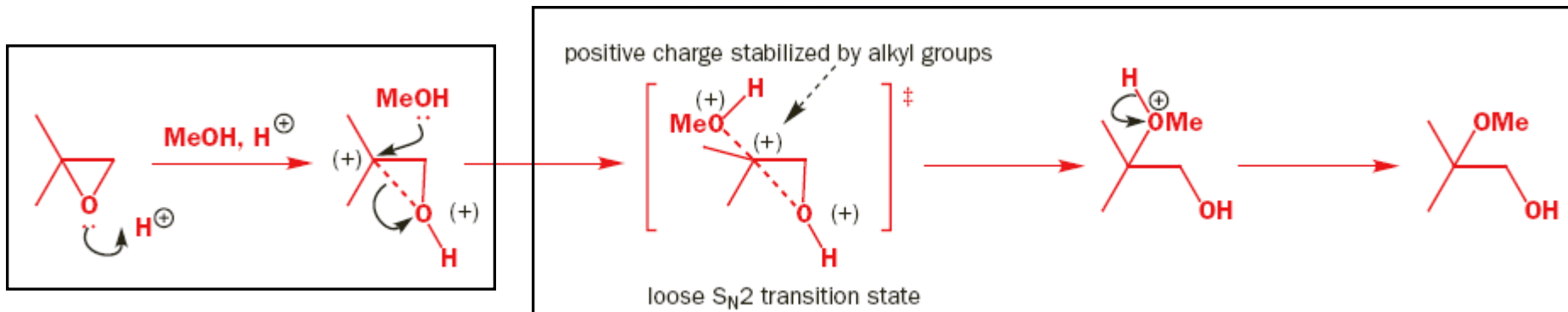
mechanizmusok

nukleofil támadás – protonálás nélkül az epoxid oxigén rossz távozó csoport: erős nukleofil kell és a sztérikus hatások lesznek a döntőek

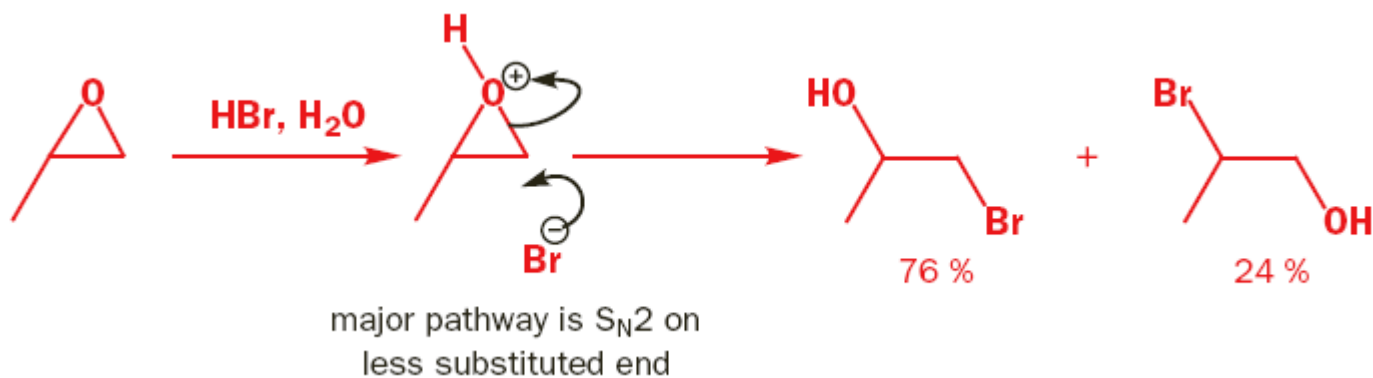


tiszta $\text{S}_{\text{N}}2$ reakció

protonálás először, majd nukleofil támadás



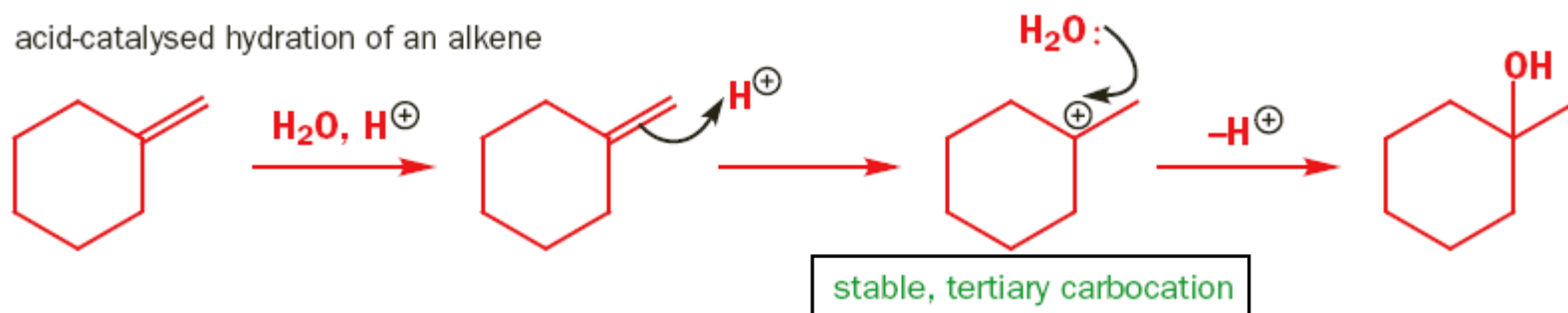
azért akadnak zavarok



vízaddíció

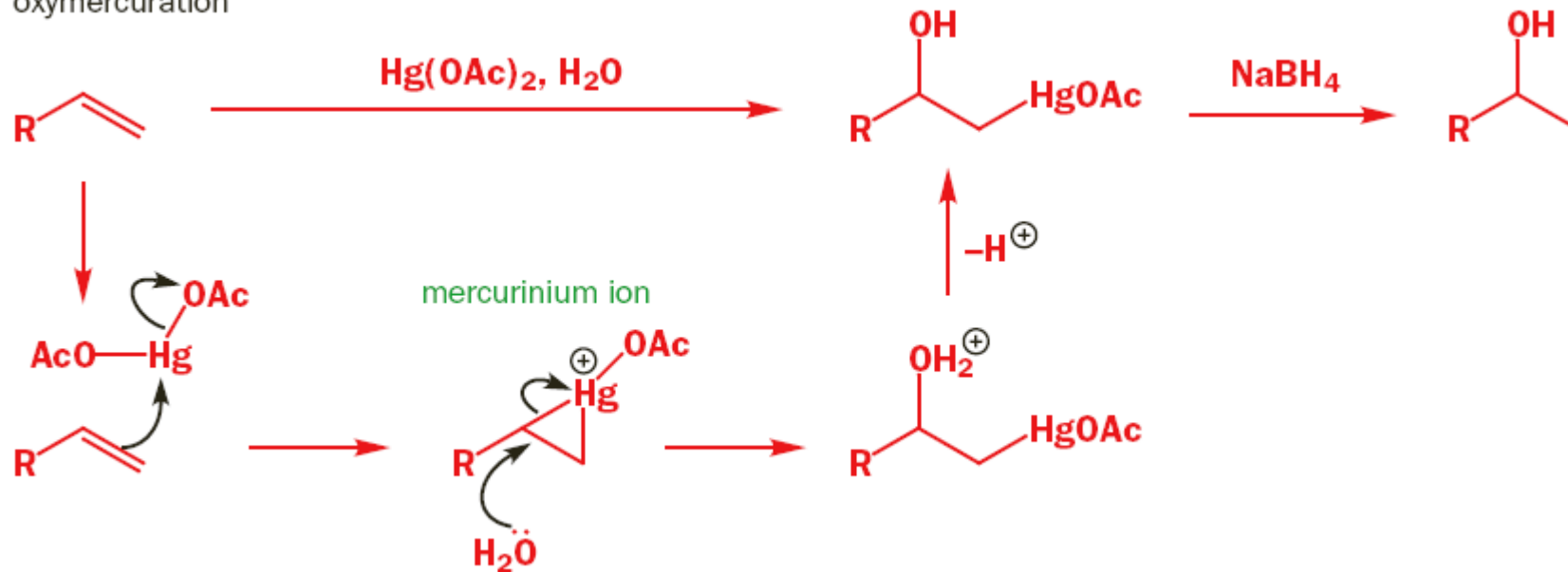
mehet direkt módon is

acid-catalysed hydration of an alkene



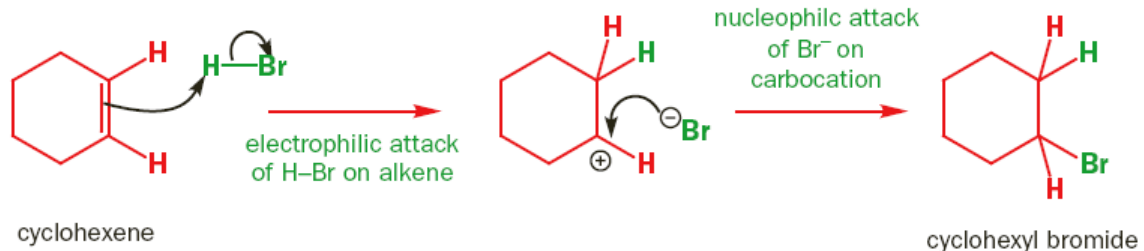
de többnyire katalitikus

oxymercuration

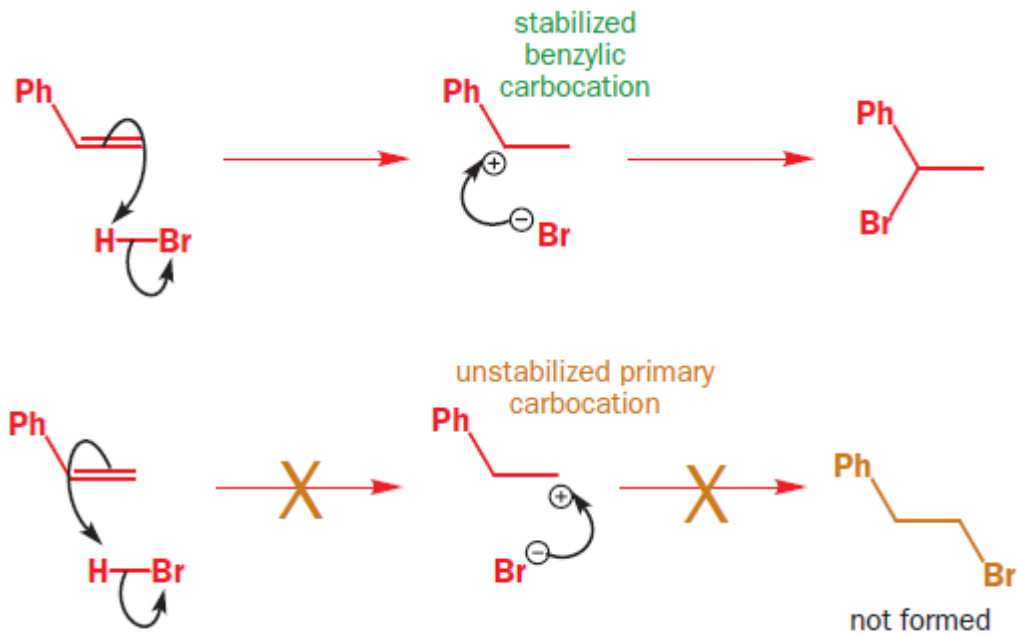


HBr addíció

electrophilic addition of HBr to cyclohexene



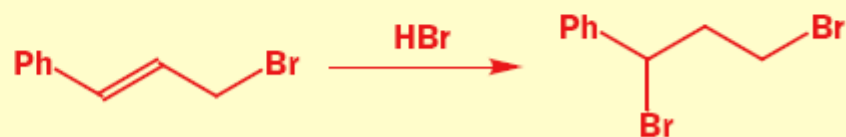
a HBr addíció régioszelektív



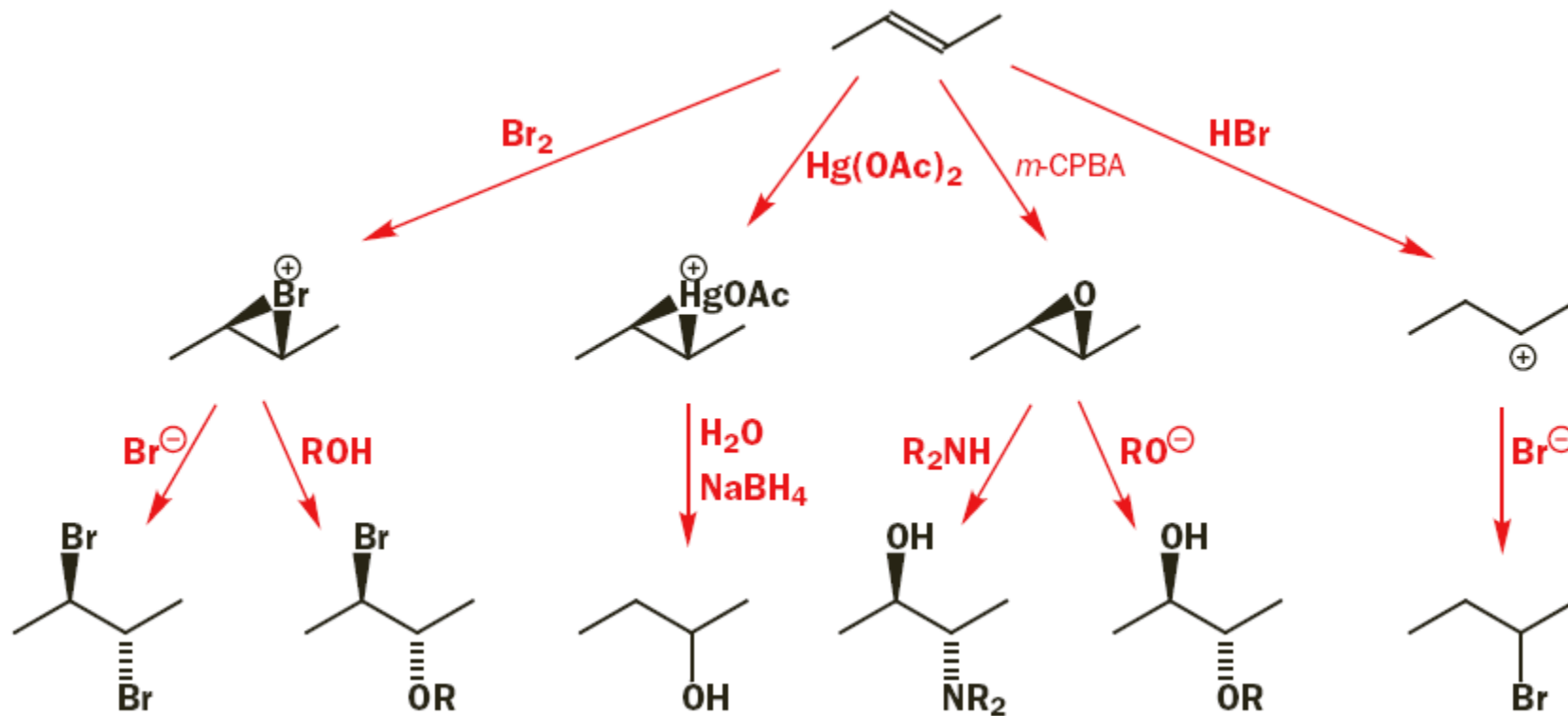
Markovnikov's rule

There is a traditional mnemonic called 'Markovnikov's rule' for electrophilic additions of H-X to alkenes, which can be stated as 'The hydrogen ends up attached to the carbon of the double bond that had more hydrogens to start with.' We don't suggest you learn this rule, though you may hear it referred to. As with all 'rules' it is much

more important to understand the reason behind it. For example, *you* can now predict the product of the reaction below. Markovnikov couldn't.



Összefoglalás



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