TÁMOP-4.1.1.F-14/1/KONV-2015-0006
SZTE TTIK, KTCS, 1a) Duális és moduláris képzésfejlesztés a mesterképzéshez

Nukleofil addíció karbonilcsoportra

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020
MAGYARORSZÁG KORMÁNYA
Európai Unió
Európai Szociális Alap
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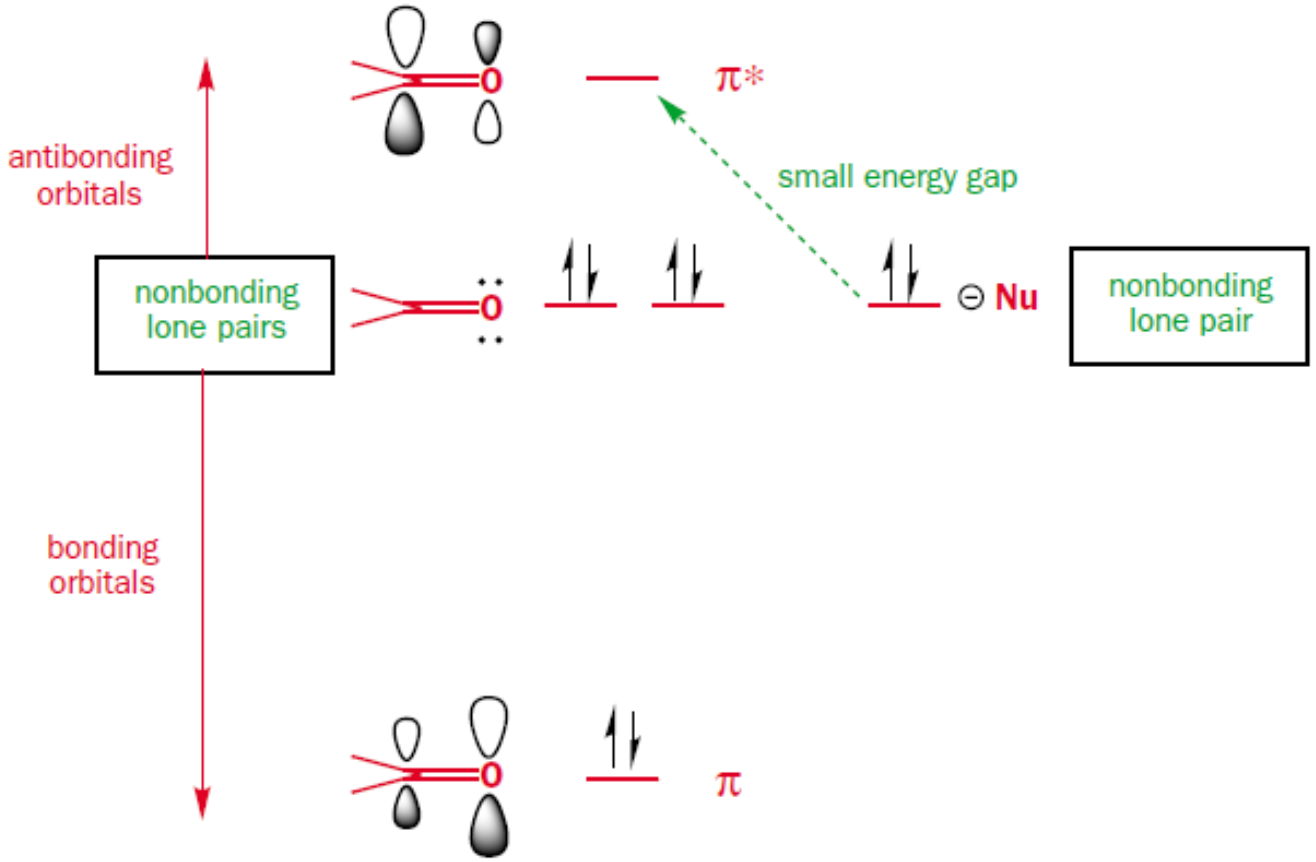
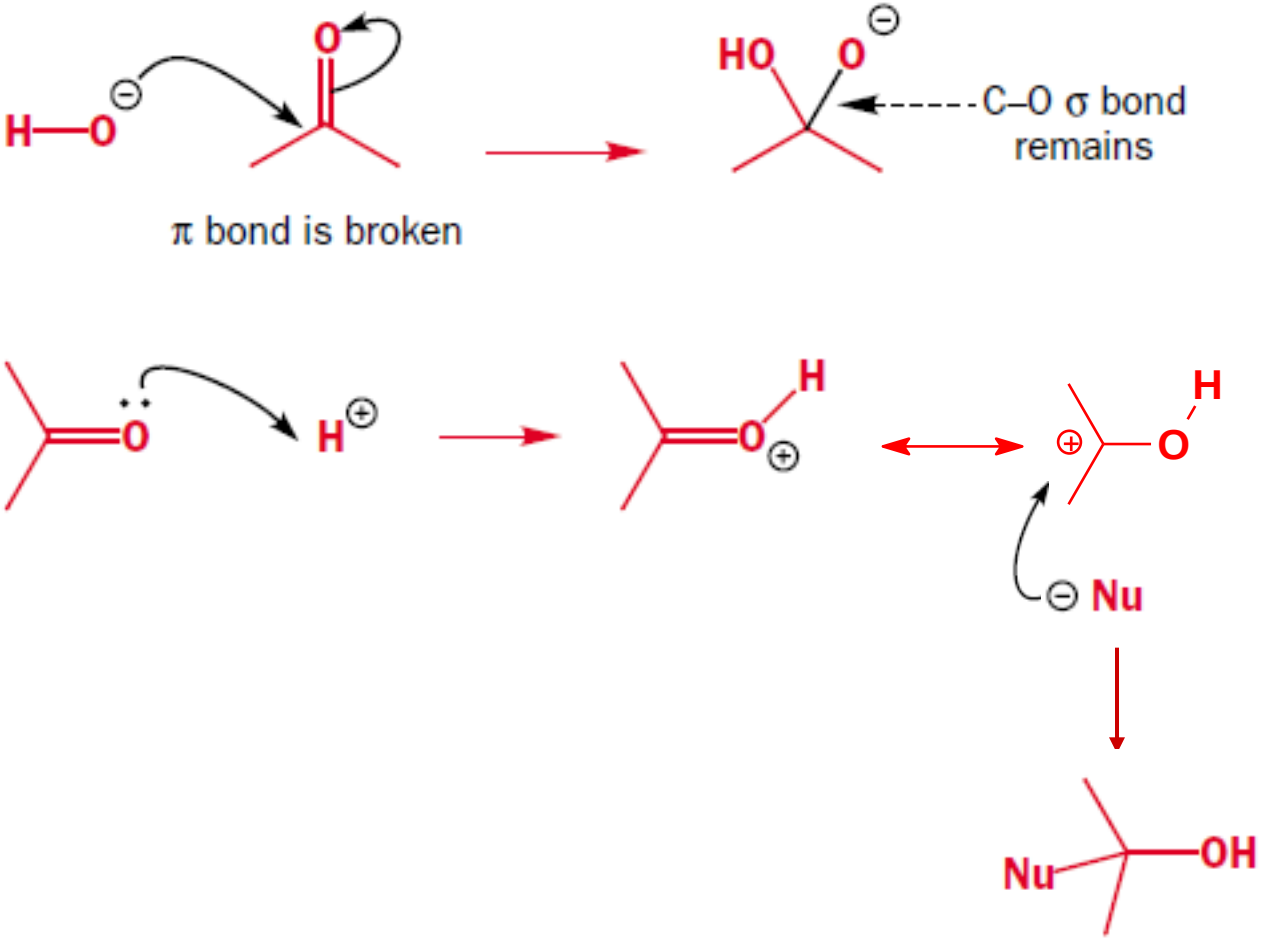
a karbonilcsoport és a nukleofil elektronrendszere és a közöttük létrejövő kölcsönhatás az MO elmélet szerint

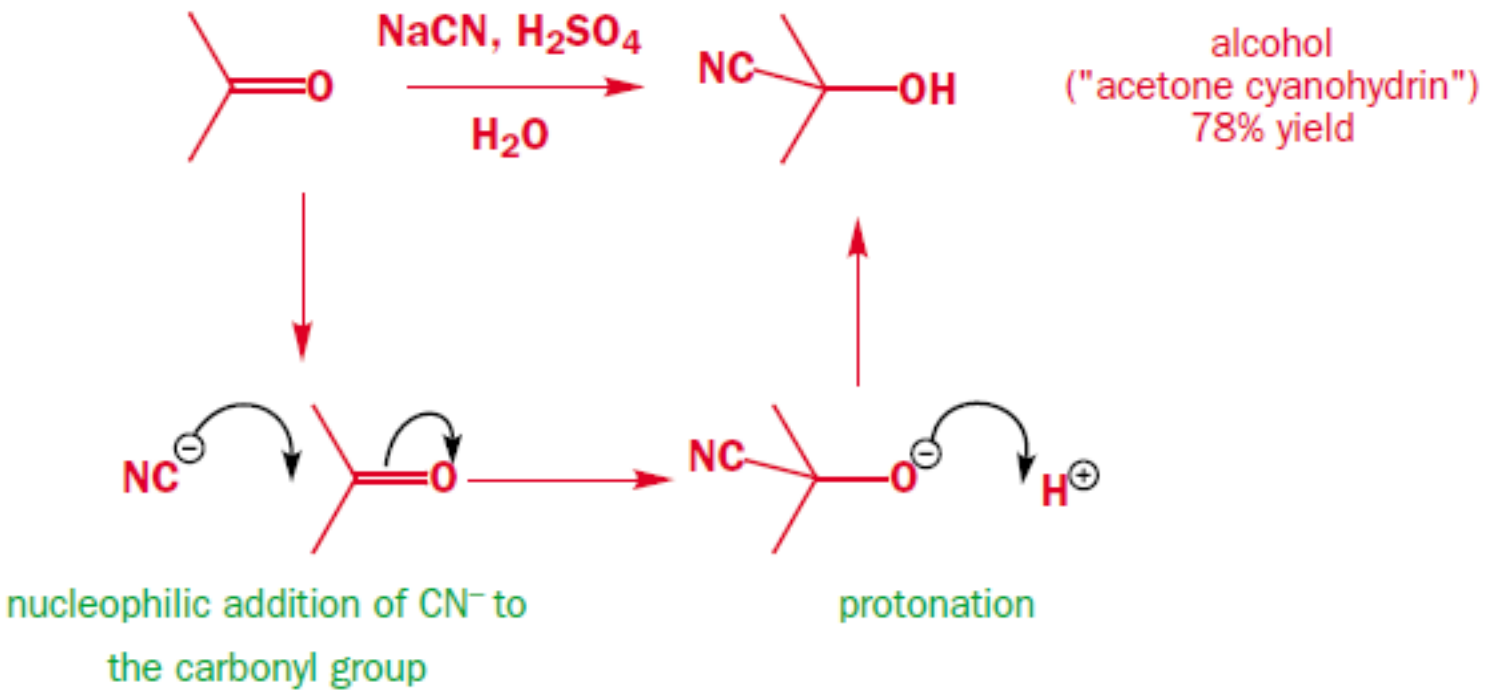


HOMO (a nukleofilé)–LUMO (a karbonilcsoporté) kölcsönhatás

a karbonilcsoport és a nukleofil kölcsönhatása a VB elmélet szerint



egy működő példareakció

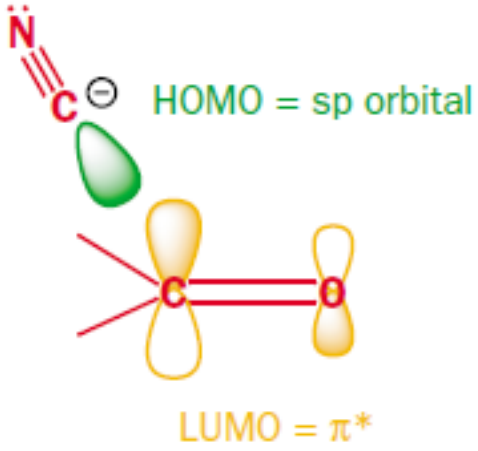


Additions to carbonyl groups generally consist of two mechanistic steps:

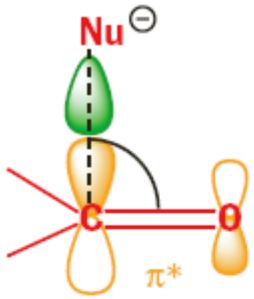
1 Nucleophilic attack on the carbonyl group

2 Protonation of the anion that results

a kölcsönhatásban résztvevő molekulapályák

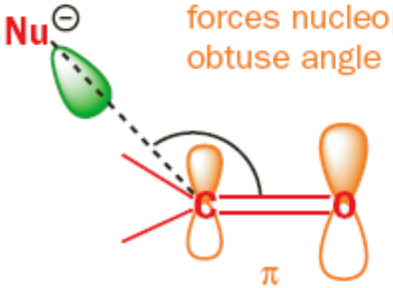


a Bürgi-Dunitz szög



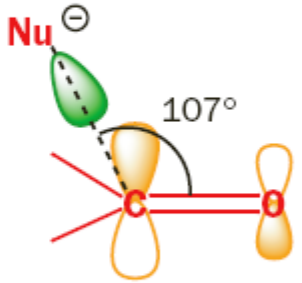
maximum overlap with π*
perpendicular to C=O bond

repulsion from filled π orbital
forces nucleophile to attack at
obtuse angle



combined effect:

nucleophile attacks
C=O at 107° angle

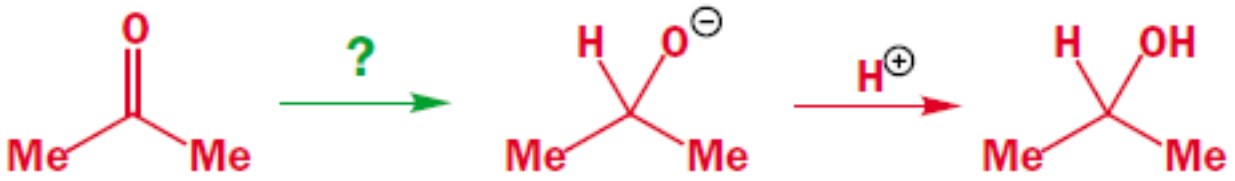


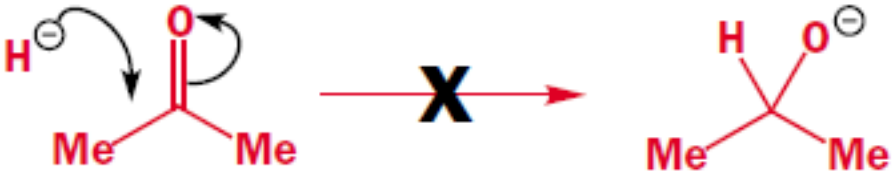
The Bürgi–Dunitz angle

Bürgi and Dunitz deduced this trajectory by examining crystal structures of compounds containing both a nucleophilic nitrogen atom and an electrophilic carbonyl group. They found that, when the two got close enough to interact, but were not free to undergo reaction, the nitrogen atom always lay on or near the 107° trajectory decribed here. Theoretical calculations later gave the same 107° value for the optimum angle of attack.

egy fontos reakció

reduction of a ketone to an alcohol

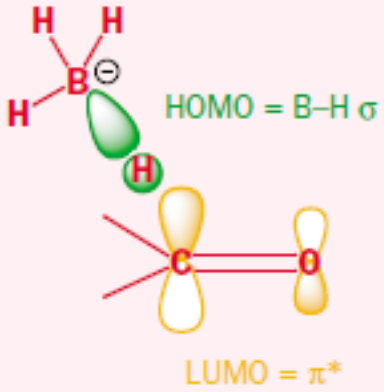




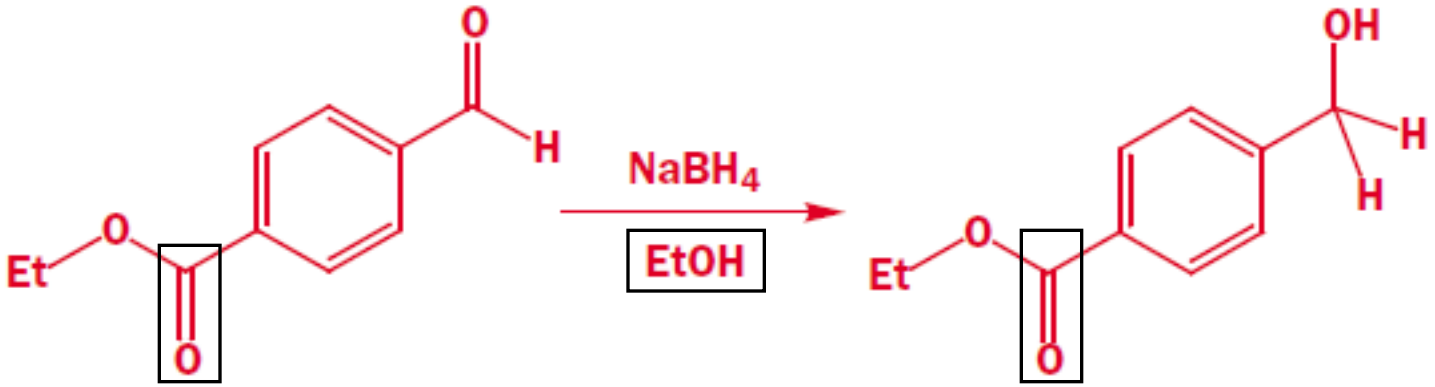
nucleophilic attack by H^-
never happens

H^- *always* reacts as a base

The reason that H^- never acts as a nucleophile is that its 1s orbital is too small. The orbitals involved in borohydride reductions are the π^* of the C=O group as the LUMO and a B–H σ orbital as the HOMO, so there is a much better orbital match.

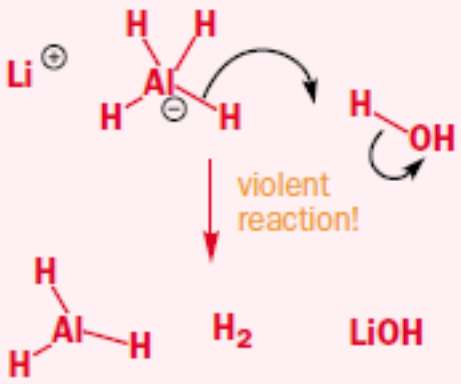


a $NaBH_4$ szelektív reagens (a kevésbé reaktív karbonilcsoporttal nem reagál), és lehet protikus oldószerben használni

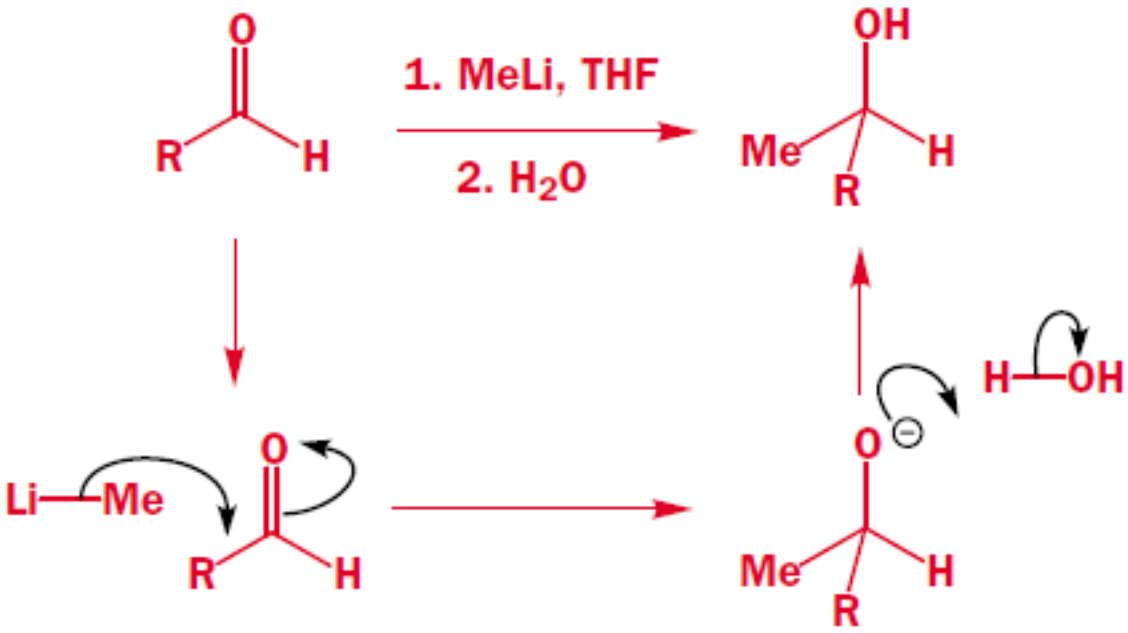


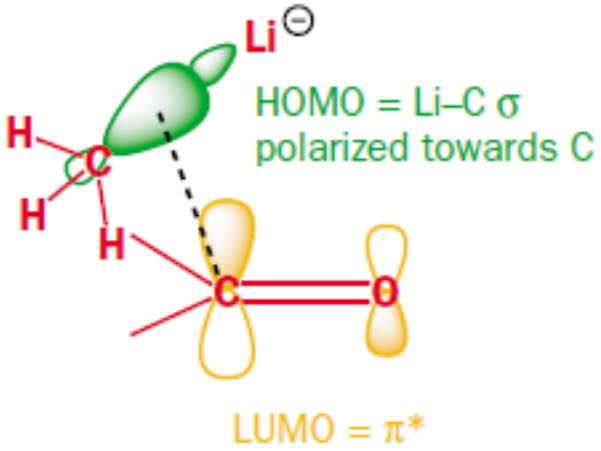
a $LiAlH_4$ erőteljesebb, ezért kevesbé szelektív reagens, és nem lehet protikus oldószeben használni

Aluminium is more electropositive (more metallic) than boron and is therefore more ready to give up a hydrogen atom (and the associated negative charge), whether to a carbonyl group or to water. Lithium aluminium hydride reacts violently and dangerously with water in an exothermic reaction that produces highly flammable hydrogen.

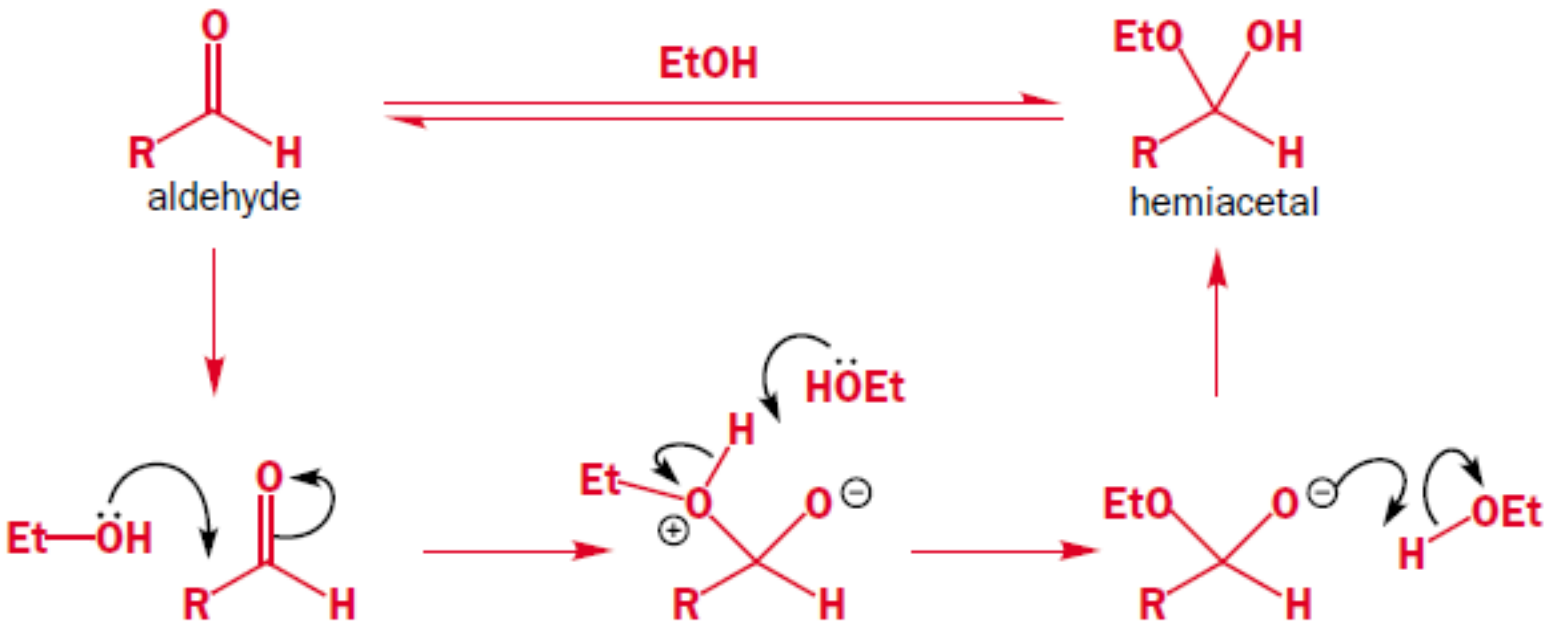


még egy fontos reakció

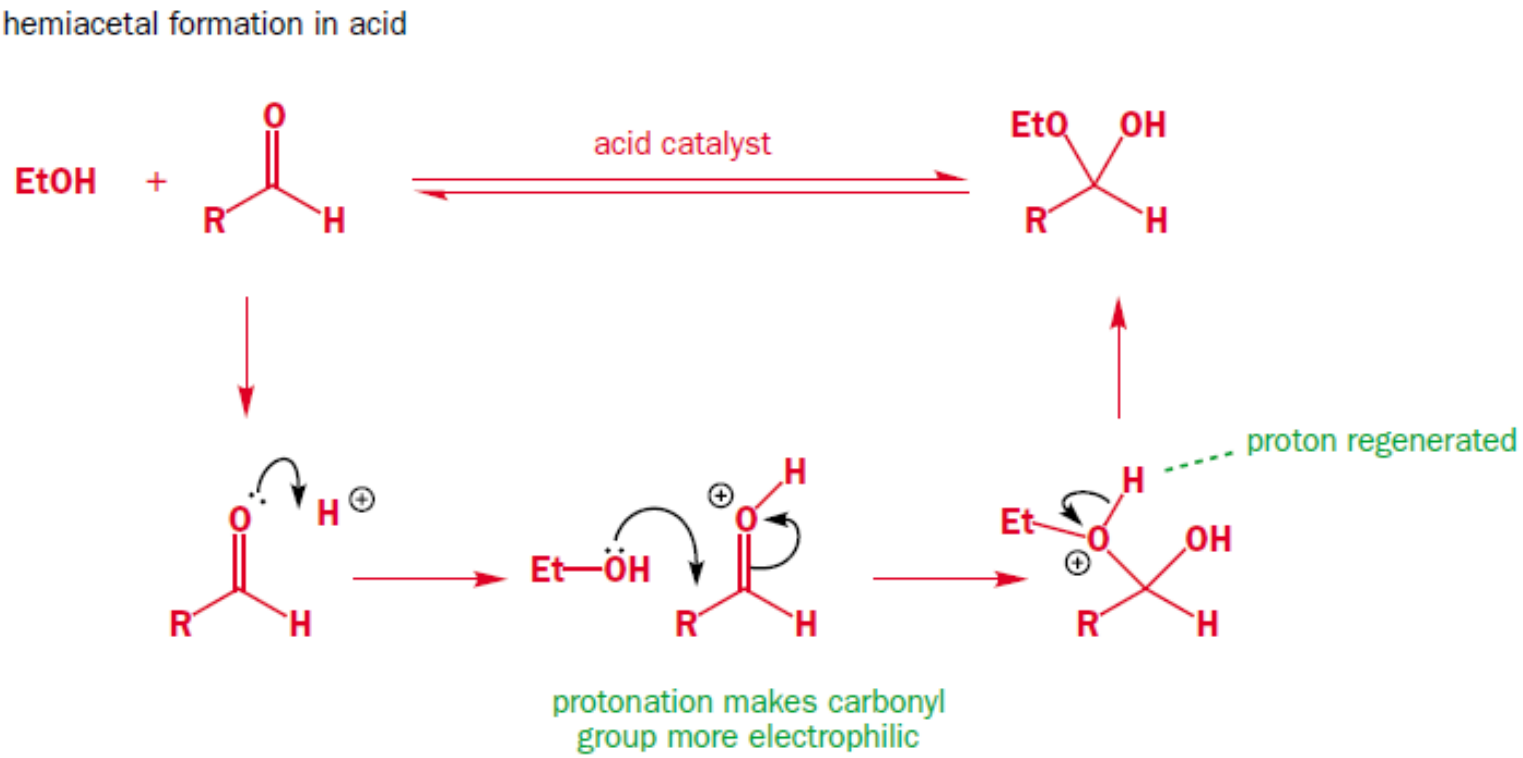




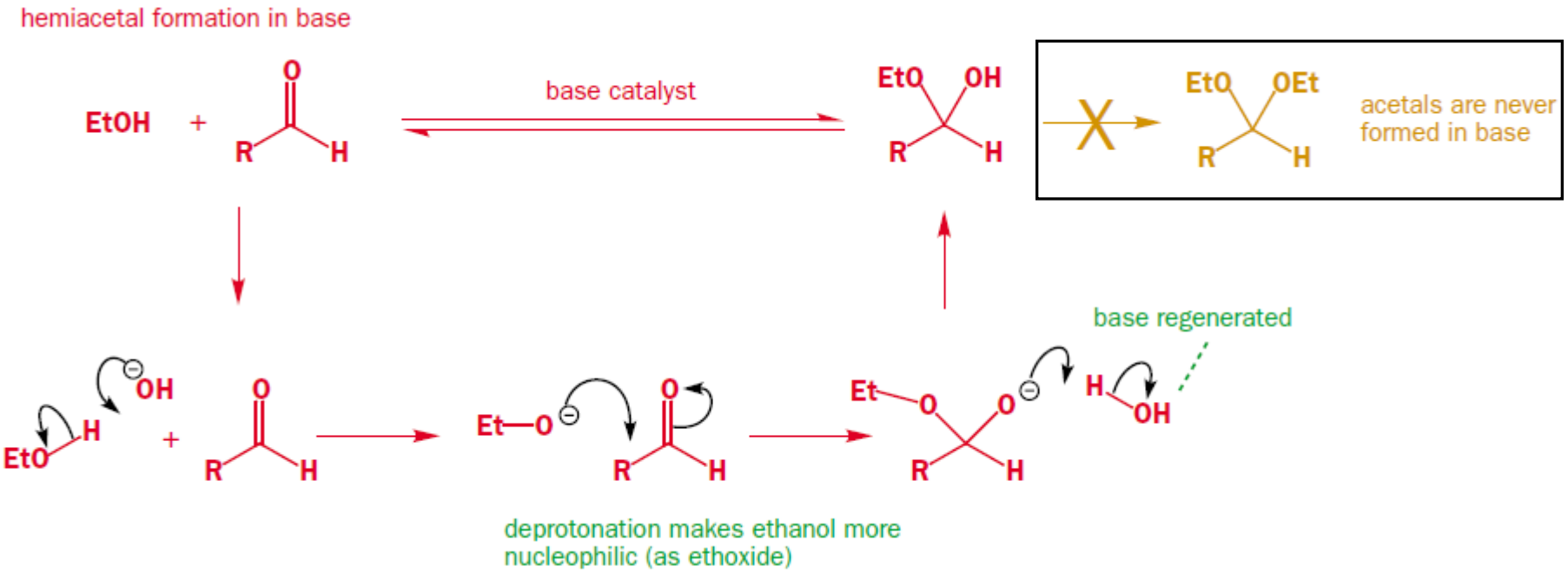
nameg még egy



lehet savkatalizált



és lehet báziskatalizált is

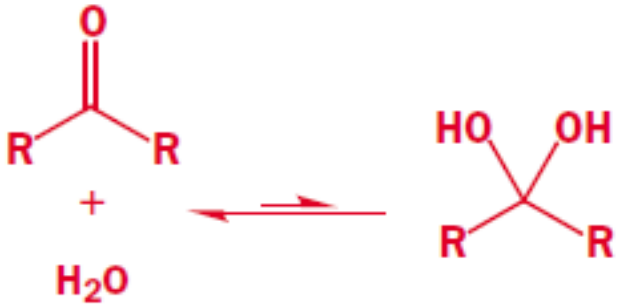


ezt csinálja a bázis

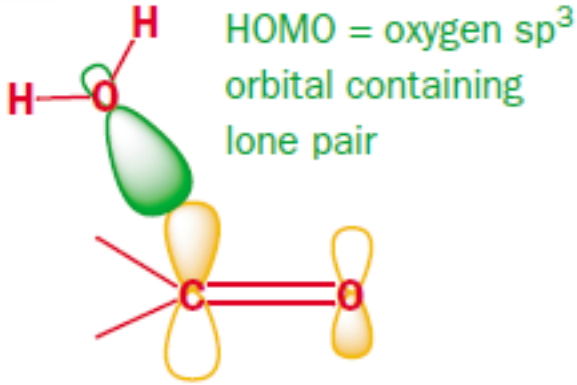
For nucleophilic additions to carbonyl groups:

- Acid catalysts work by making the carbonyl group more electrophilic
- Base catalysts work by making the nucleophile more nucleophilic

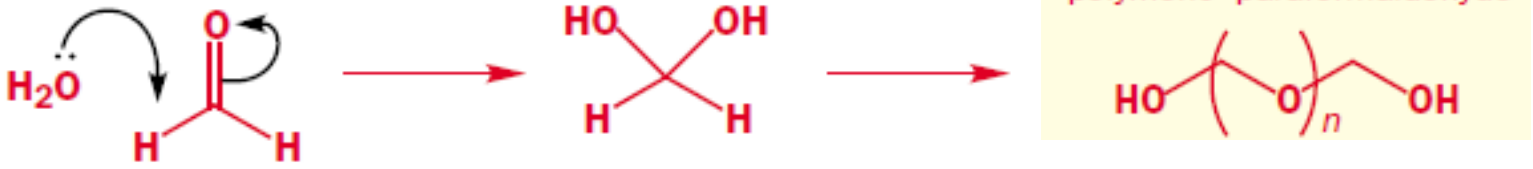
a félacetálképzés egy "alváltozata"

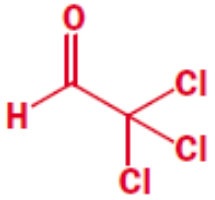
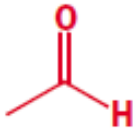
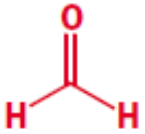
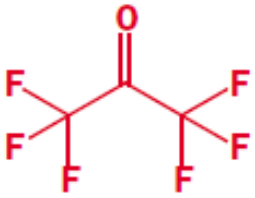


significant concentrations of hydrate are generally formed only from aldehydes

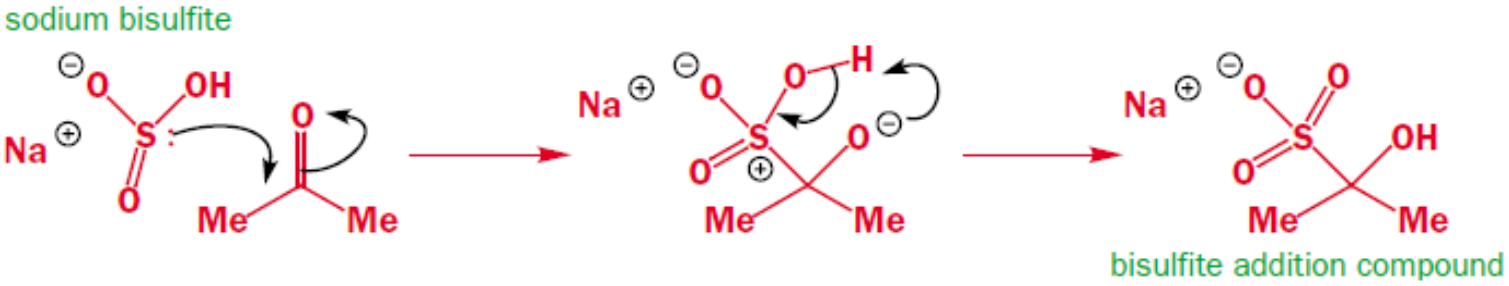


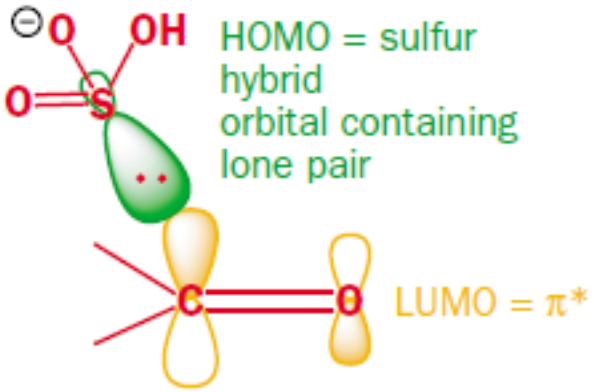
orbitals involved in the addition of water



		equilibrium constant *K*			
acetone		0.001	chloral		2000
acetaldehyde		1.06			
formaldehyde		2280	hexafluoroacetone		1 200 000

ez már tényleg az utolsó





orbitals involved in the addition of bisulfite

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