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

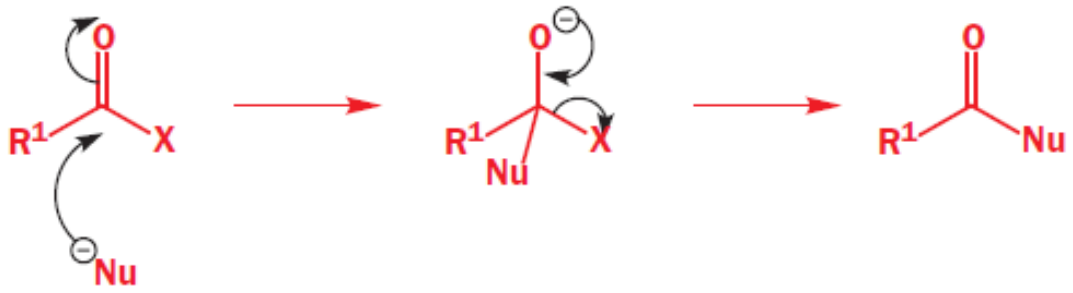
Nukleofil szubsztitúciós reakciók 3. Nukleofil szubsztitúció a karbonilszénen, a karboniloxigén elvesztésével

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020
Magyarország Kormánya
Európai Unió
Európai Szociális Alap
BEFEKTETÉS A JÖVŐBE

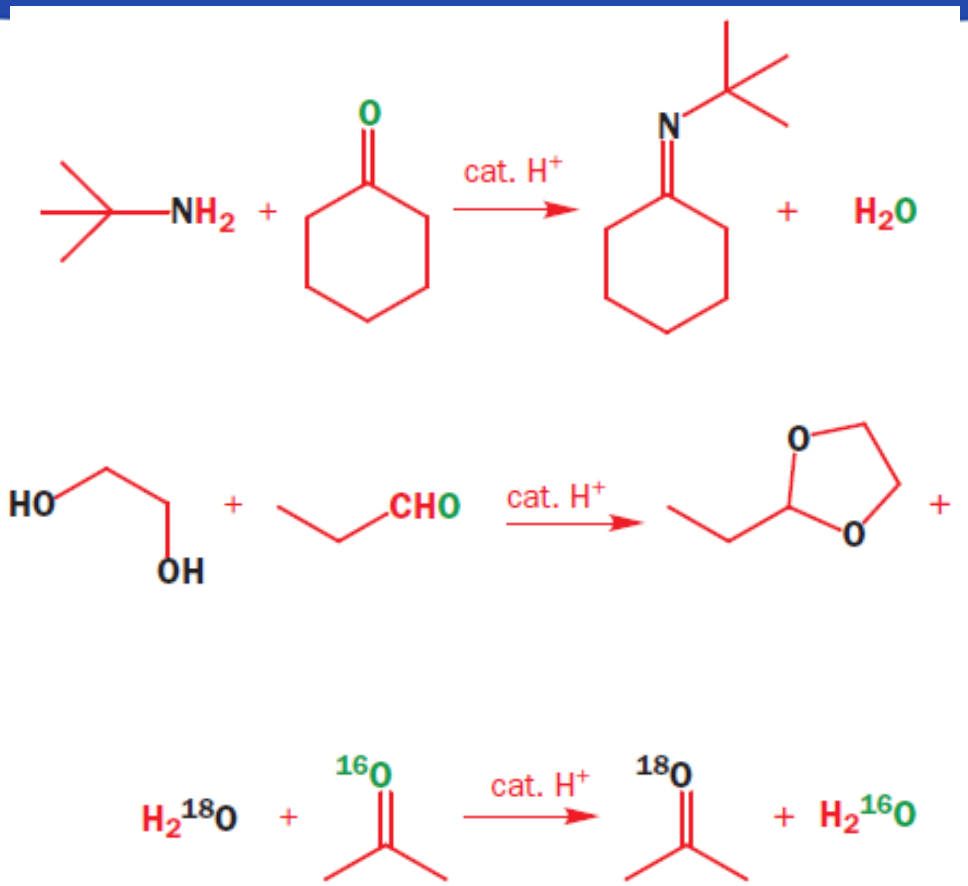
eddig ilyet láttunk

nucleophilic substitution
at a carbonyl group

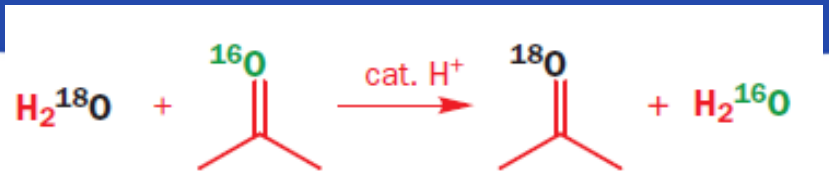


nukleofil acilszubsztitúció, avagy nukleofil szubsztitúció a karbonilszénen

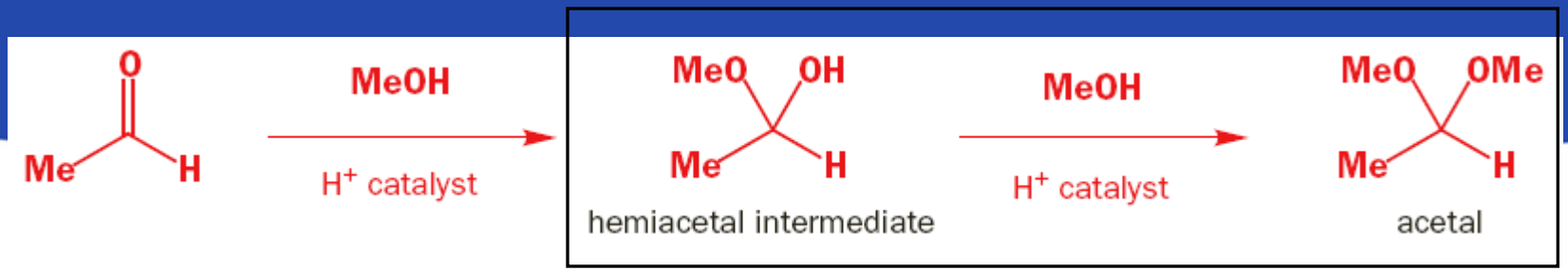
most ilyeneket fogunk



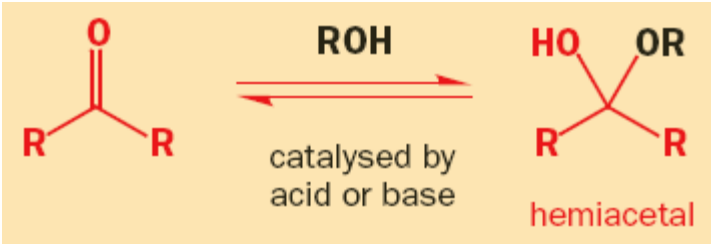
nukleofil szubsztitúció a kabonilszénen,a karboniloxigén elvesztésével



az egyensúly erőteljesen balra tolódik

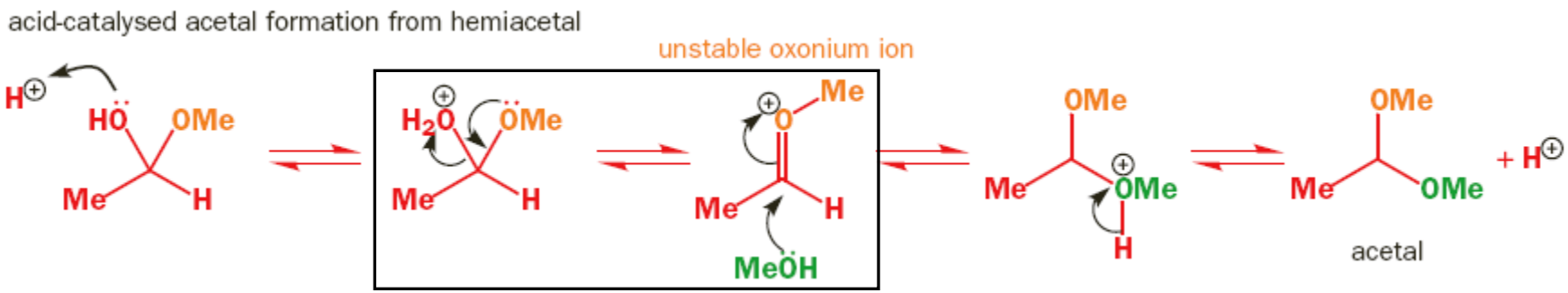


nukleofil szubsztitúció



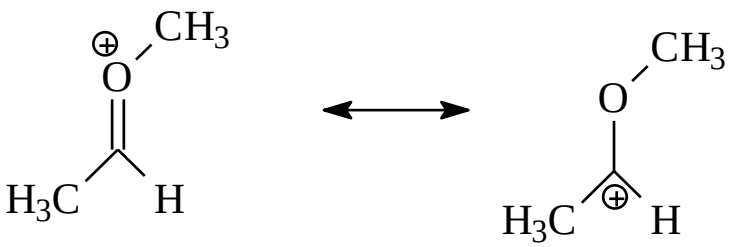
nukleofil addíció

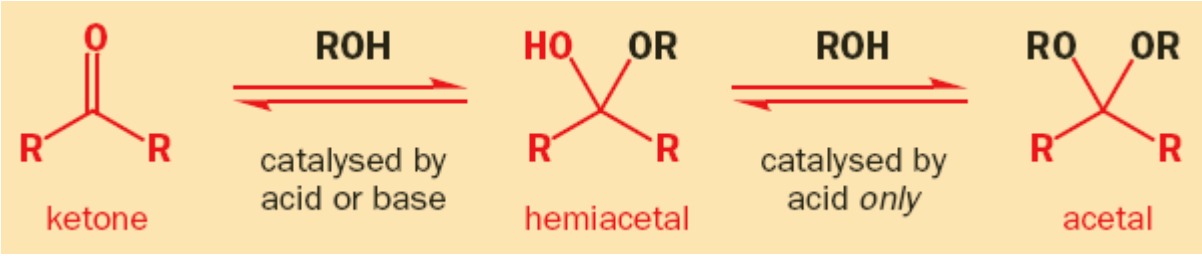
a nukleofil szubsztitúció mechanizmusa



ebben a lépésben veszett el
a karboniloxigén

a kulcsintermedier

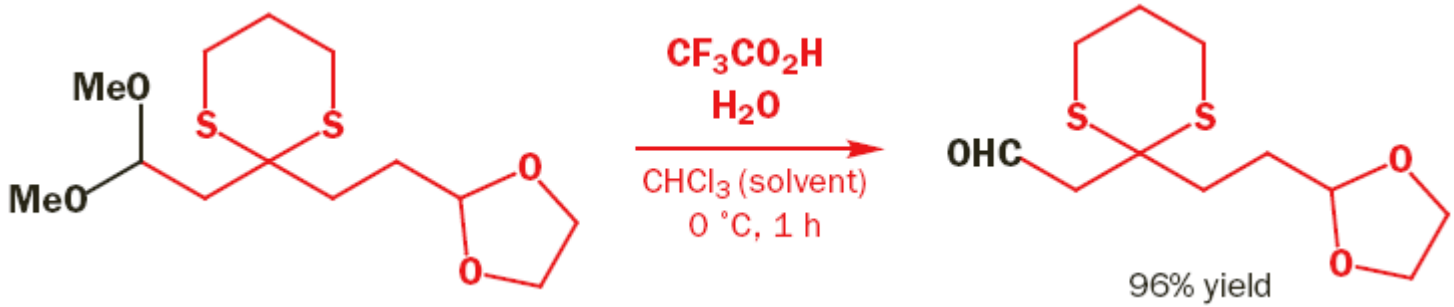




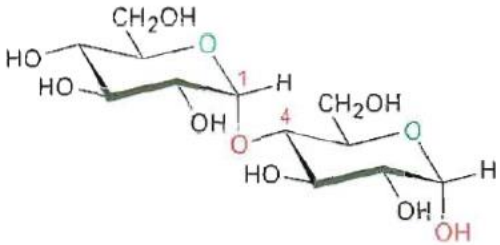
Acetal hydrolysis

Acetals can be hydrolysed in acid but are stable to base.

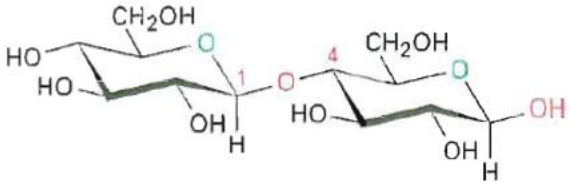
legfontosabb felhasználás: védőcsoport (inkább ciklikus acetál)



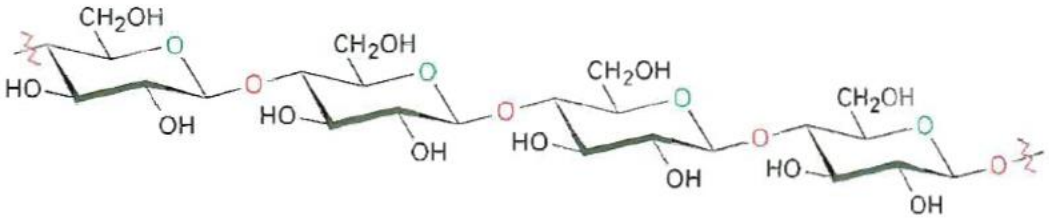
a természet legfontosabb acetáljai



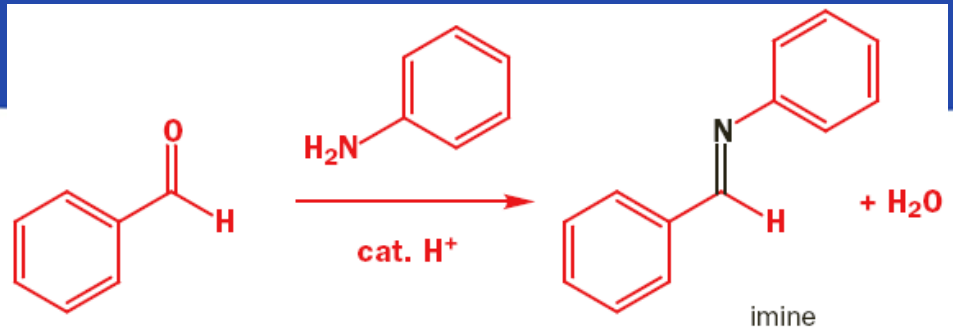
Maltose, a 1 → 4-α-glycoside

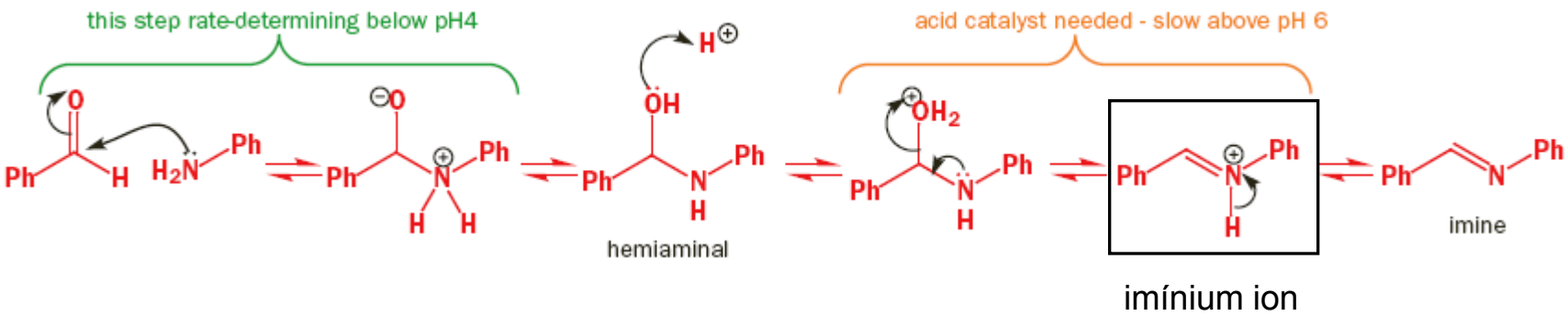


Cellobiose, a 1 → 4-β-glycoside

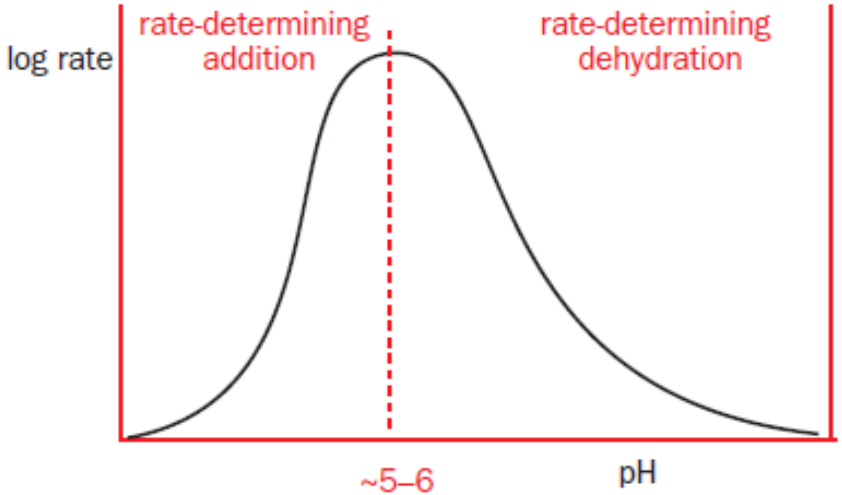


Cellulose, a 1 → 4-*O*-(β-D-glucopyranoside) polymer

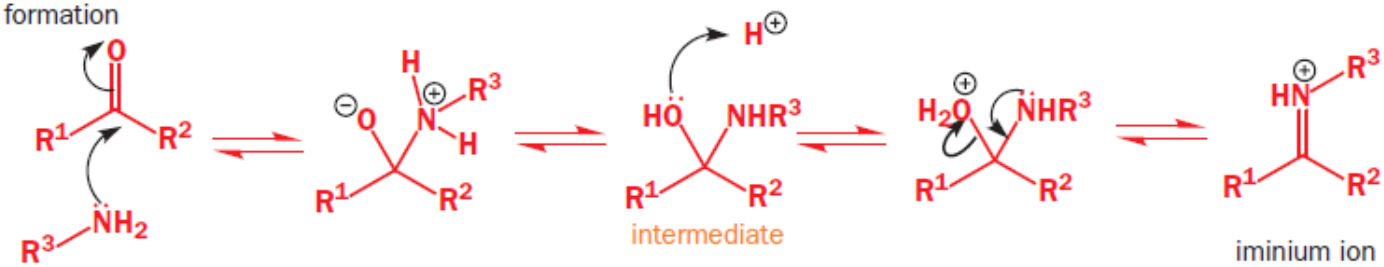

O
H
H_2N
cat. H^+
N
H
+ H_2O
imine


this step rate-determining below pH4
acid catalyst needed - slow above pH 6
O
Ph
H
H_2N
Ph
O
Ph
N
H
H
Ph
$H^{\oplus}$
OH
Ph
N
H
Ph
hemiaminal
OH_2
Ph
N
H
Ph
Ph
N
H
Ph
Ph
N
Ph
imine

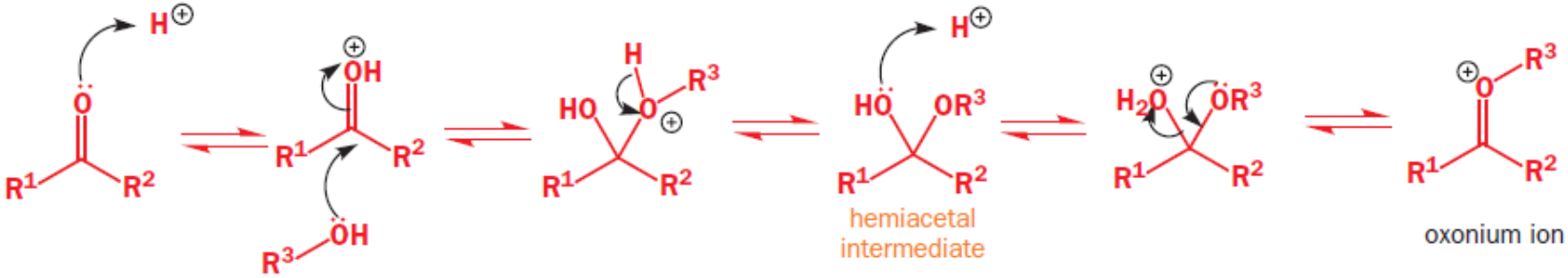
imínium ion

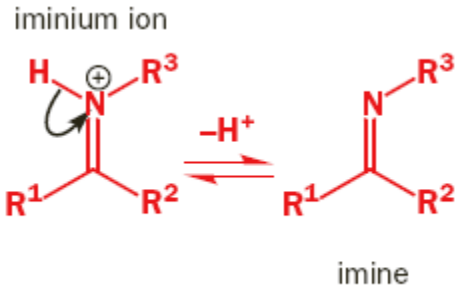

log rate
rate-determining
addition
rate-determining
dehydration
~5–6
pH

acid-catalysed imine formation

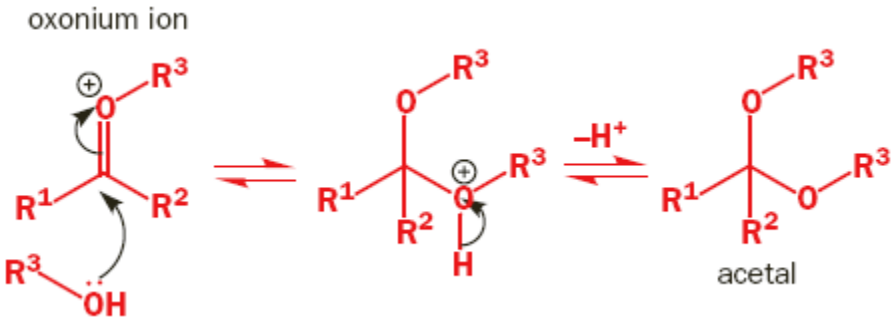


acid-catalysed acetal formation





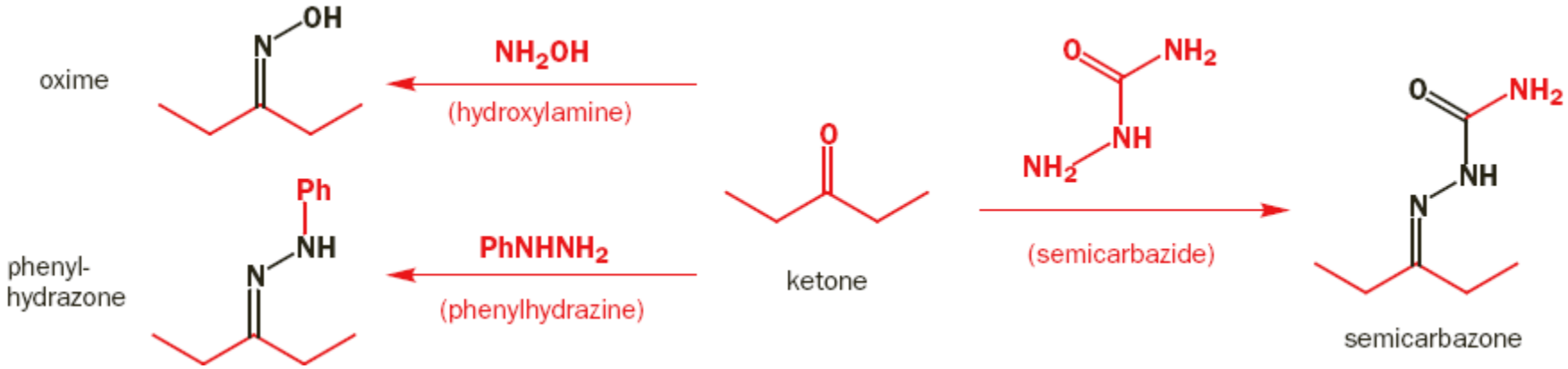
savként viselkedik - deprotonálódik



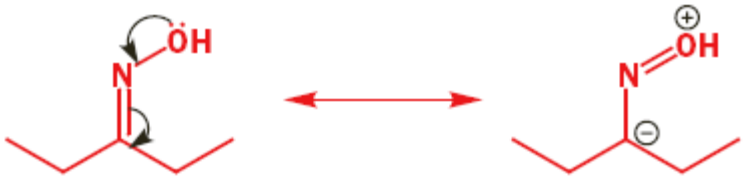
elektrofilként viselkedik

az iminek általában kevéssé stabilisak, hidrolízisük sokszor még sav- vagy bázis-katalízis nélkül is jól megy

az oximok, hidrazonok és szemikarbazonok viszont stabilisak

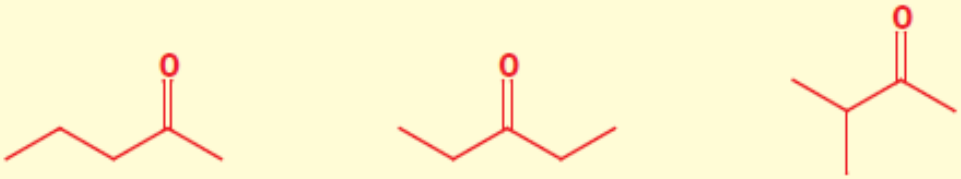


az ok: rezonanciastabilizálás



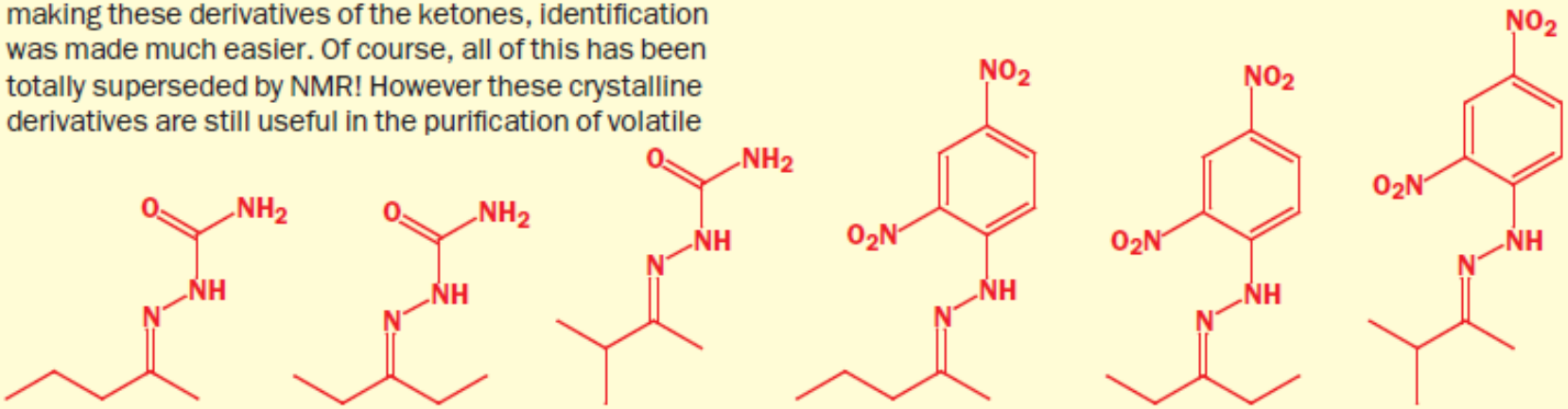
Historical note

Because the hydrazone and semicarbazone derivatives of carbonyl compounds are often stable, crystalline solids, they used to be used to confirm the supposed identity of aldehydes and ketones. For example, the boiling points of these three isomeric five-carbon ketones are all similar, and before the days of NMR spectroscopy it would have been hard to distinguish between them.

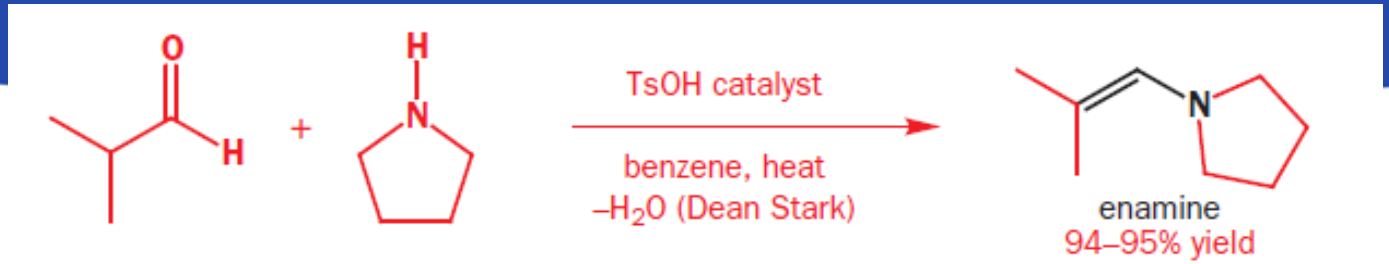


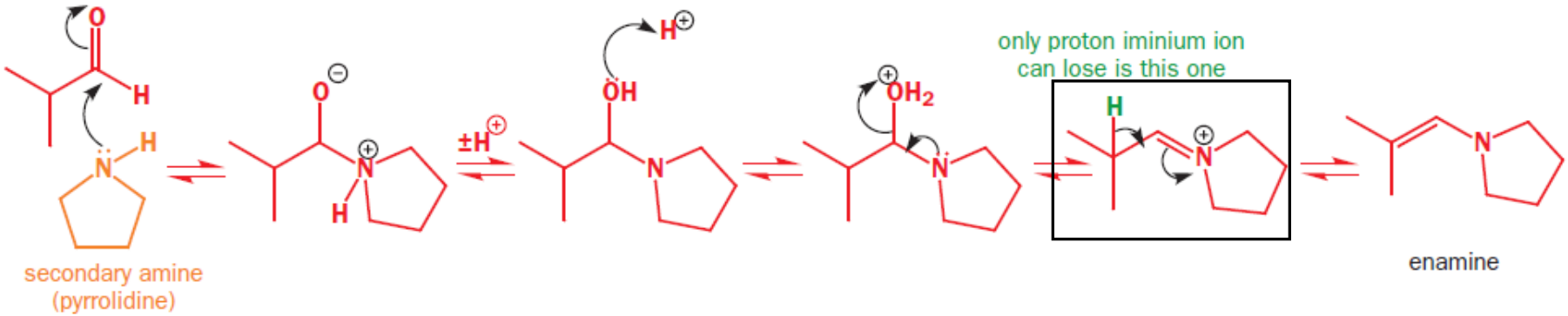
b.p. 102 °C b.p. 102 °C b.p. 106 °C

Their semicarbazones and 2,4-dinitrophenylhydrazones, on the other hand, all differ in their melting points. By making these derivatives of the ketones, identification was made much easier. Of course, all of this has been totally superseded by NMR! However these crystalline derivatives are still useful in the purification of volatile aldehydes and ketones and in solving structures by X-ray crystallography.

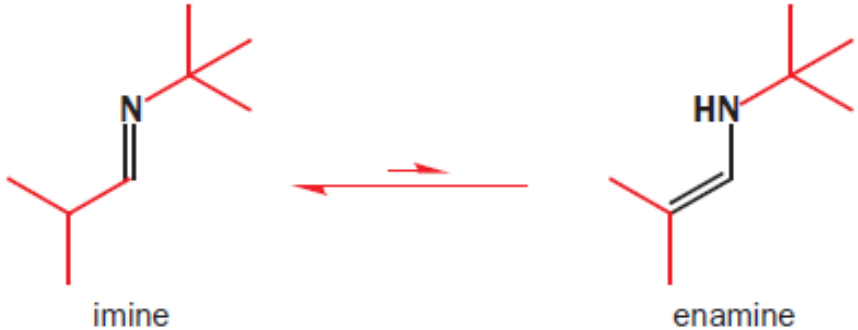


m.p. 112 °C m.p. 139 °C m.p. 157 °C m.p. 143 °C m.p. 156 °C m.p. 125 °C



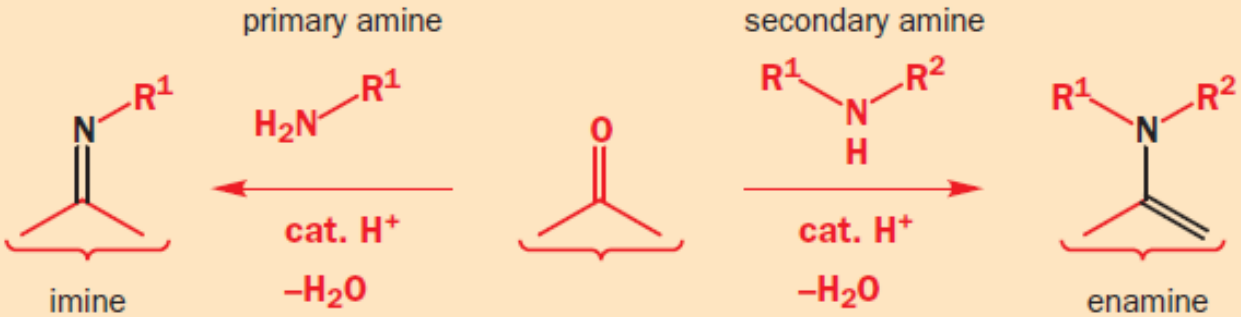


a "röndös" imin is tartalmaz némi énamint



Imines and enamines

- Imines are formed from aldehydes or ketones with primary amines
- Enamines are formed from aldehydes or ketones with secondary amines
- Both require acid catalysis and removal of water



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