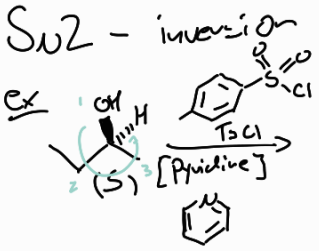
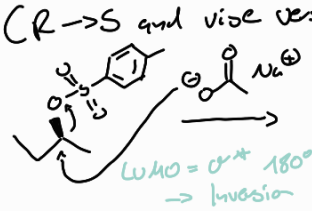
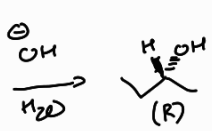
Stereochem

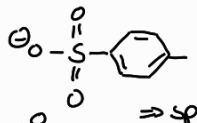
S_N2 – inversion (R → S and vice versa)

ex

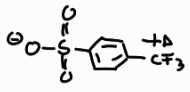


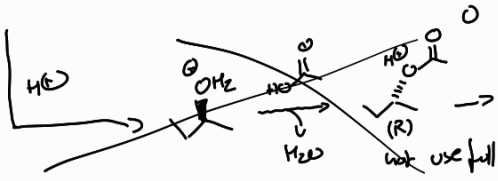




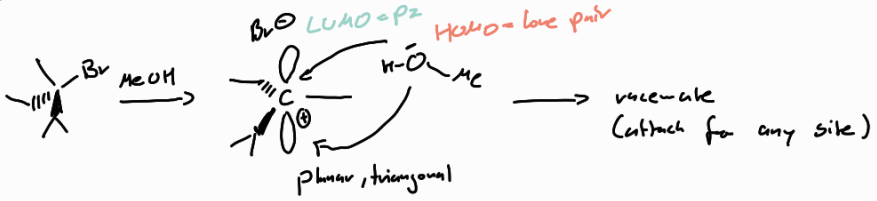


⇒ speed up reaction, making TsO^- an even better LG e.g.:





S_N1 racemizes

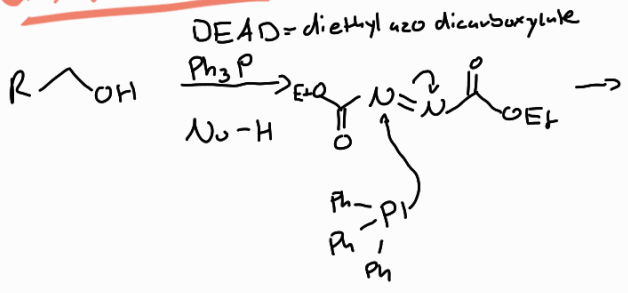


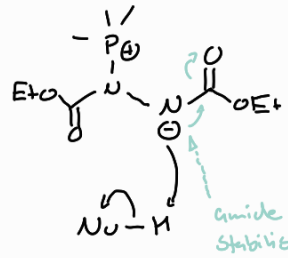
TIP

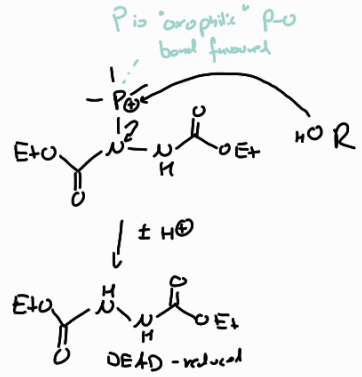
p. 347 reactivity table

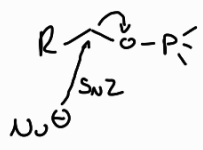
1. Ts ✓
2. Acid ✓
3. Mitsunobu

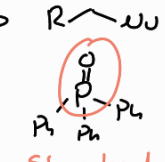
DEAD = diethyl azo dicarboxylate





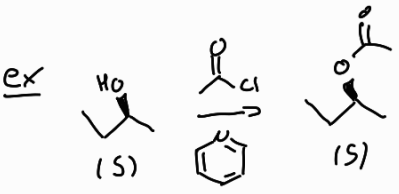


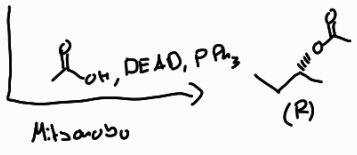




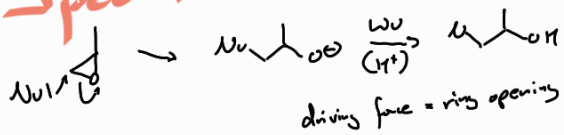
Strong bond, gain in free engy

ex





Special LG ⇒ epoxide



driving force = ring opening

Hard vs Soft Nu

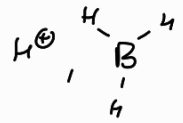
Hard

Small
charged
basic
low Energy HOMO
like C=O
ex: $^{\ominus}OH$, $RO^{\ominus}$, $^{\ominus}NH_2$
R-Li

Soft

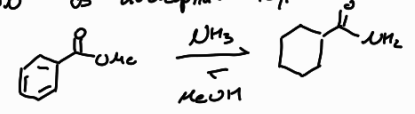
Larger
neutral
non basic
high Energy HOMO
like sp^3
$R-S^{\ominus}$, RSH, $I^{\ominus}$
R_3P, alkene

also HSAB (hard soft acid base)

hard: $H^{\oplus}$, 

Soft: Hg^{2+}, $Br_3^{\oplus}$, Br_2

S_N2 vs nucleophilic acyl substitution

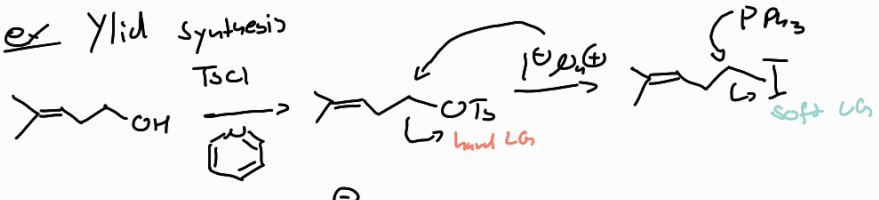
ex 

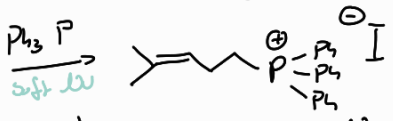
NH_3 is a better Nu than MeOH
$NH_2^{\ominus}$ worse LG than MeOH
(nucleophilicity ≈ basicity)

S_N2 different

ex $I^{\ominus}$ higher HOMO reacts well with σ^* on alkyls
so $I^{\ominus}$ is a good Nu and a good LG

ex Ylid synthesis

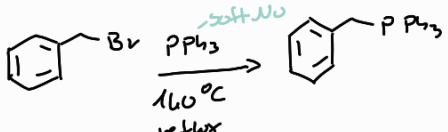




→ Iodine reacts as Nu and LG

→ Using Iodine prevents the usage of hard LG with soft Nu. This (hard + soft) would lead to a lower Yield.
=> Use Soft - Soft and hard - hard

different example:



→ with LiI 2h at rt, since $I^{\ominus}$ is softer than $Br^{\ominus}$

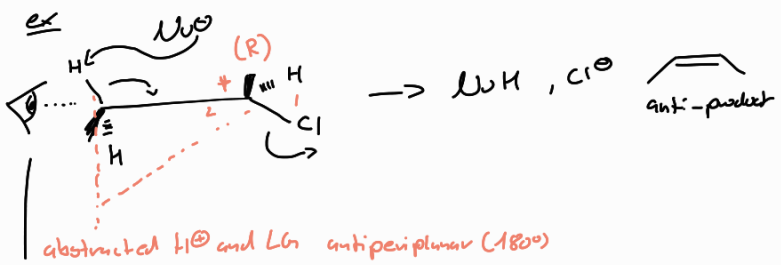
Eliminations Ch 17 E_2, E_1, (Ecb)

$Nu^{\ominus}$ acts as a base and abstract $H^{\oplus}$ at β-carbon

E_2 = bi-molecular

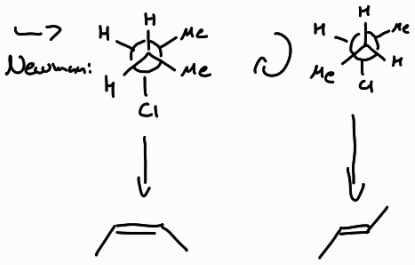
rate = $k[Nu^{\ominus}][\text{halide}]$ see below

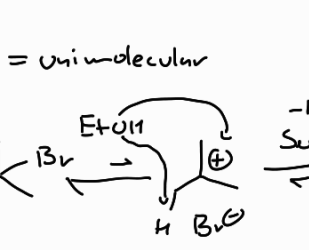
ex



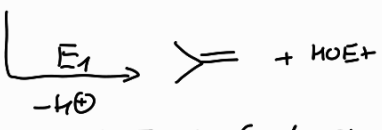
abstracted H⊕ and LG antiperiplanar (180°)

→ Newman:





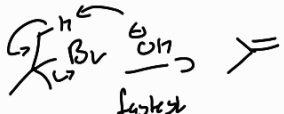
E2 = unimolecular



→ competing reaction, if E1 > Sn1 stronger base

$^{\ominus}OEt$ faster than HOEt if the base becomes stronger

E2 is more favored



fastest

To avoid Sn1 completly use

Strong Bulky Base