Substitution reactions: SN1 vs SN2

- Organic Chemistry 1, lecture 9
- Sample deck written by Exam Twin. Not from a real class.

SN2: one step

- The nucleophile attacks as the leaving group leaves, in one concerted step
- Backside attack inverts the stereocenter (Walden inversion)
- Rate = k[substrate][nucleophile], so SN2 is second order

SN2: what speeds it up

- Substrate: methyl > primary > secondary; tertiary does not react by SN2
- Bulky groups block the backside attack (steric hindrance)
- Strong nucleophiles and polar aprotic solvents (DMSO, acetone, DMF) favor SN2

SN1: two steps

- Step 1, the slow step: the leaving group leaves and a carbocation forms
- Step 2: the nucleophile attacks the flat carbocation from either face
- Rate = k[substrate], so SN1 is first order: the nucleophile is not in the rate law

SN1: what speeds it up

- Carbocation stability: tertiary > secondary, and primary almost never
- Polar protic solvents (water, methanol, ethanol) stabilize the carbocation
- Weak nucleophiles are fine, because they are not part of the slow step

Stereochemistry

- SN2 at a stereocenter gives inversion of configuration
- SN1 gives a mix of both configurations (racemization), often with a little more inversion

Leaving groups

- Good leaving groups are weak bases: I- > Br- > Cl- >> F-
- OH- is a poor leaving group until it is protonated to water
- Tosylate (OTs) is an excellent leaving group

Exam tip

ON THE EXAM

- On the exam: decide SN1 or SN2 from the substrate, nucleophile and solvent
- Carbocation rearrangements (hydride and methyl shifts) only happen in SN1