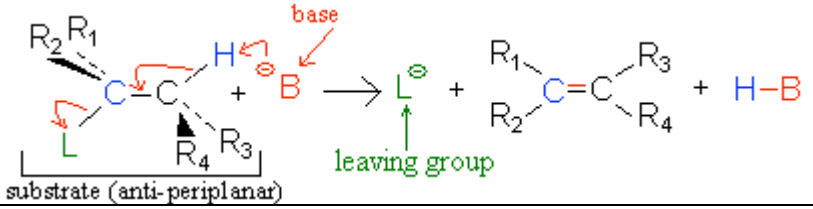
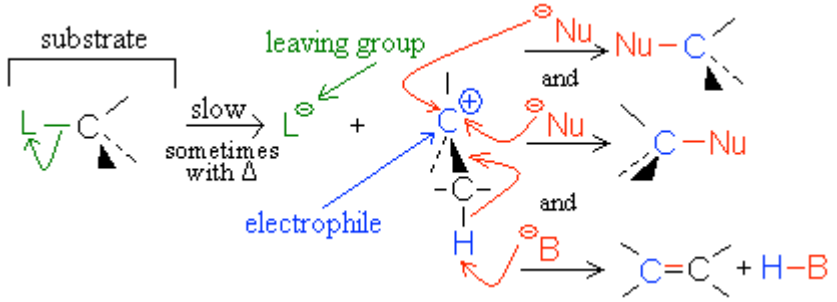
S_N2

E2



S_N1/E1



S_N1 and E1 have identical rate determining steps, so they generally occur simultaneously and have the same properties.

	S_N2 and E2	**S_N1/E1**
mechanism	one step—this single step is the rate-determining step (RDS)	two steps—RDS is formation of carbocation
big obstacle	S_N2: steric hindrance blocking Nu (Nu is in RDS) E2: blocking B isn't a big obstacle (B doesn't join substrate)	stabilizing carbocation (Nu/B isn't in RDS, so blocking it isn't an obstacle)
stereo-chemistry	S_N2: inversion (backside attack, since LG blocks frontside) E2: cis vs. trans determined by anti-periplanar transition-state	S_N1: racemization (planar carbocation intermediate) E1: both cis and trans isomers will be produced
regio-chemistry	E2: possible products from deprotonation of any β-carbon major product w/ bulky base: less substituted (steric hindrance) major product with non-bulky base: more substituted	E1: possible products from deprotonation of any β-C major product: more substituted alkene (e^--donating alkyl substituents stabilize alkenes)
rate expression	Rate = k [substrate] [Nu^- or B^-], so [Nu^-/B^-] ↑ → rate ↑ (substrate and Nu^-/B^- are in RDS)	Rate = k [substrate], so [Nu^-/B^-]↑ → rate unchanged (only the substrate is in RDS)
Nu quality	requires good Nu/strong B (Nu/B is in RDS) bulky Nu/B favors E2 vs. S_N2 (blocking B isn't a big obstacle)	can work with a poor Nu/weak B (Nu/B isn't in RDS)
LG quality	requires good leaving group (because leaving group is in RDS)	requires good leaving group (because LG is in RDS)
preferred solvent?	polar aprotic (no O-H or N-H bonds) (for S_N2, hydrogen-bonds to solvent would block Nu) (for E2, protic solvent would protonate the base)	polar protic (at least one O-H or N-H bond) (hydrogen-bonds to solvent stabilize carbocation)
substrate	S_N2: methyl>1°>2°; 3° gives no S_N2 (substitutents block Nu) E2: 1°, 2°, or 3° (blocking B is not a big obstacle)	3° > 2°; methyl and 1° give no S_N1/E1 (alkyl substituents stabilize the carbocation)

comparing the same element

	charge	**resonance**
nucleophilicity	negative charge → better Nu	resonance → worse Nu (charge is stabilized)
basicity	negative charge → stronger base	resonance → weaker base (charge is stabilized)
leaving-group ability	positive charge → better LG (more willing to accept electrons)	resonance → better LG (charge will be stabilized)

comparing different elements

	same row	**same column**
big difference	electronegativity	size
nucleophilicity	less electronegative → better Nu (willing to donate electrons)	bigger → better Nu (usually) (big Nu's are less hindered by solvent, more polarizable)
basicity	less electronegative → stronger base (willing to donate electrons)	bigger → weaker base (large base can spread out and stabilize electron density)
leaving-group ability	more electronegative → better LG (willing to accept electrons)	bigger → better leaving group (big LG's can spread out and stabilize electron density)

nucleophiles, leaving groups, bases

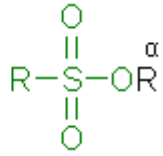
nucleophiles

N	O	~~F~~	N^-	O^-	~~F^-~~	good Nu (S_N2 or S_N1)
P	S	~~Cl~~	P^-	S^-	Cl^-	poor Nu (S_N1 only)
	Se	~~Br~~		Se^-	Br^-	~~not a Nu~~
		~~I~~			I^-	

cyanide NC^- (charge on the C) azide N_3^-

leaving groups

~~N~~	~~O~~	~~F~~	N^+	O^+	good LG
~~P~~	~~S~~	Cl	P^+	S^+	~~not a LG~~
		Br			
		I			

sulfonate 

The α carbon is attached to the oxygen, not to the sulfur.

bases

N	O	~~F~~	N^-	O^-		strong base (E2)
P	S	~~Cl~~	P^-	S^-	Cl^-	weak base (E1)
		~~Br~~			~~Br^-~~	~~not a base~~
		~~I~~			~~I^-~~	

Nucleophiles and bases shown with charges before attacking.
Leaving groups shown with charges before leaving.
The tables for individual atoms assume no resonance. Resonance makes atoms into worse nucleophiles and bases and into better leaving groups.

what happens in S_N2, S_N1, E2, and E1 mechanisms

	what happens	**big obstacle**
S_N2	One step: Nucleophile joins α carbon and leaving group leaves α carbon	steric hindrance
S_N1	Step one: Leaving group leaves α carbon Step two: Nucleophile joins α carbon	stabilizing the carbocation
E2	One step: Base takes β hydrogen, π bond forms between α and β carbons, leaving group leaves α carbon.	none
E1	Step one: Leaving group leaves α carbon Step two: Base takes β hydrogen, π bond forms between α and β carbons	stabilizing the carbocation

how to determine S_N2 vs. E2 vs. S_N1 vs. E1 for haloalkane and alkylsulfonate substrates

	poor Nu / weak base O with no formal charge	**good Nu / weak base** Cl^-, Br^-, I^-, NC^-, N_3^-, S^-, Se^-, or CH_3COO^- or N, S, or Se with no formal charge	**good Nu / strong base** N^- , O^-
methyl α-carbon **1° α-carbon**	no reaction	S_N2 [1]	E2 with *tert*-butyl-oxide (bulky base) [2] Otherwise, S_N2
2° α-carbon	95% S_N1 5% E1 (usually not shown)	S_N2 [1]	E2
3° α-carbon	95% S_N1 5% E1 (usually not shown)	95% S_N1 5% E1 (usually not shown)	E2

For cases with "95% S_N1, 5% E1", E1 products are generally not shown unless the problem specifies "all possible products".

[1] No reaction if beta-carbon is 4°.
[2] S_N2 for methyl α-carbon.

The table displays the major reaction(s) for each case—in some cases there may be significant levels of other competing reactions.

This table may not give the correct answer in all real-world situations, but it will generally be accurate for the questions that are typical of exams.