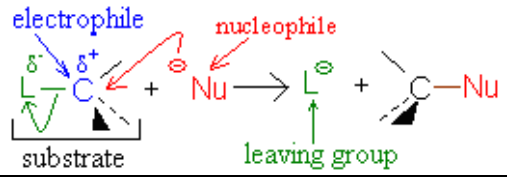
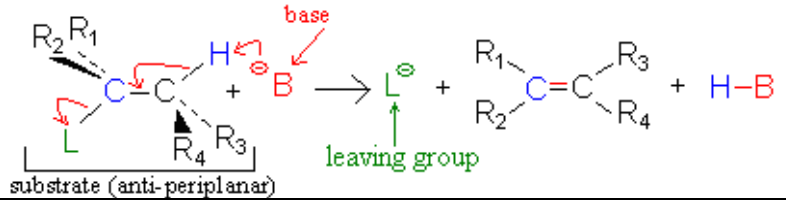
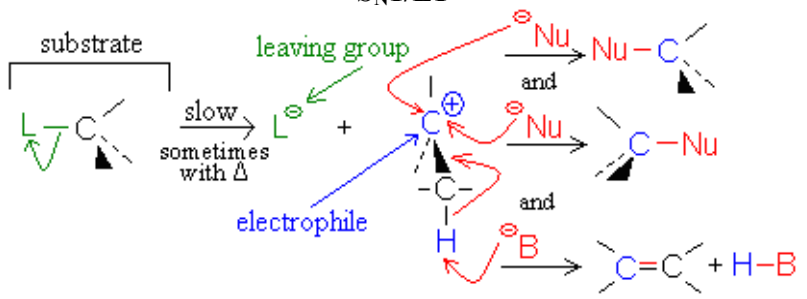
S_N2



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

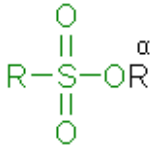
nucleophiles

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^-	weak base (E1)
		~~Br~~			~~Cl^-~~	~~not a base~~
		~~I~~			~~Br^-~~	
					~~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

S_N2	One step: Nucleophile joins α carbon and leaving group leaves α carbon
S_N1	Step one: Leaving group leaves α carbon Step two: Nucleophile joins α carbon
E2	One step: Base takes β hydrogen, π bond forms between α and β carbons, leaving group leaves α carbon.
E1	Step one: Leaving group leaves α carbon Step two: Base takes β hydrogen, π bond forms between α and β carbons

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

	poor Nu / weak base O	**good Nu / weak base** N, S, Se, Cl^-, Br^-, I^-, NC^-, N_3^-, S^-, Se^-, and acetate (CH_3COO^-)	**good Nu / strong base** N^-, O^-	
			non-bulky base	**bulky base** LDA, t-butyl-O^-
methyl α-carbon **1° α-carbon**	no reaction	S_N2 [1]	S_N2 [2]	E2 [3]
2° α-carbon	95% S_N1, 5% E1 [4]	S_N2 [1]	E2	E2
3° α-carbon	95% S_N1, 5% E1 [4]	95% S_N1, 5% E1 [4]	E2	E2

[1]No reaction if beta-carbon is 4°.
[2]E2 if beta-carbon is 3°.
[3]S_N2 for methyl α-carbon. (Methyl substrates obviously can't do elimination reactions.)
[4]For cases with "95% S_N1, 5% E1", E1 products are generally not shown unless the problem specifies "all possible products".

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.

how to determine S_N2 vs. E2 vs. S_N1 vs. E1 for alcohol substrates

First, the alcohol must be treated with an acid to give it a better leaving group.		
	"nonnucleophilic acid" + heat [1] $H_2SO_4 + \Delta$ First, acid protonates an alcohol to form a good leaving group. Then, HSO_4^- or a nonprotonated alcohol acts a base.	**"nucleophilic acid"** HCl, HBr, HI First, acid protonates alcohol to form a good leaving group. Then, Cl^-, Br^- or I^- act as nucleophiles or bases.
methyl α-carbon **1° α-carbon**	seldom tested [2]	S_N2 [3]
2° α-carbon	E1	95% S_N1, 5% E1 [4] (not S_N2) [5]
3° α-carbon	E1	95% S_N1, 5% E1 [4]

[1]When H_2SO_4 is used *without* heat, there is no reaction for methyl and 1° substrates; for 2° and 3° substrates, the mechanism is S_N1, with a nonprotonated alcohol as the nucleophile.
[2]H_2SO_4 plus heat with a methyl or 1° alcohol will give S_N2, with a nonprotonated alcohol as the nucleophile. And with very high heat and a 1° alcohol, H_2SO_4 will give E2. But these cases are seldom tested.
[3]No reaction with Cl^-.
[4]For cases with "95% S_N1, 5% E1", E1 products are generally not shown unless the problem specifies "all possible products".
[5]Recall that this case would be S_N2 for a haloalkane substrate.

Ethers have similar reactivity to alcohols. HBr and HI attack ethers in S_N2 or S_N1 mechanisms to form alcohols; with a second equivalent of acid, the alcohols can then be attacked by more HBr or HI to form haloalkanes.

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

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