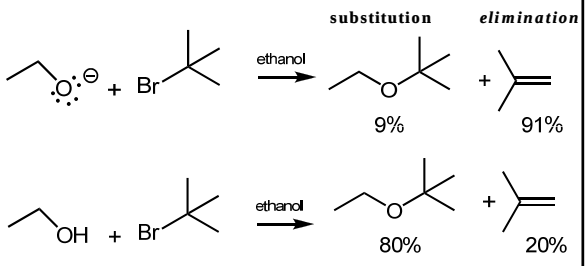
Nucleophilic Substitution Reactions

Continued

Reaction Complexity

106

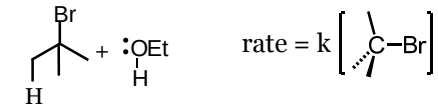
Product Mixtures

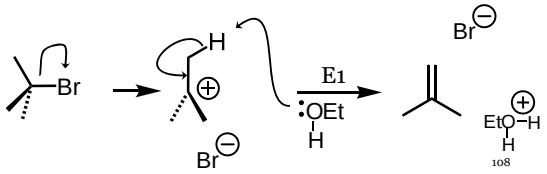


107

Reaction Mechanisms - Kinetics

E1 = Elimination 1st Order

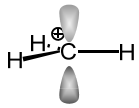




108

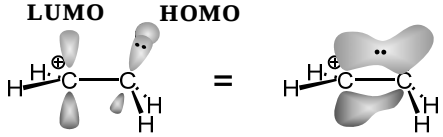
Carbocation Stabilization

Recall: Alkyl groups stabilize carbocations
hyperconjugation



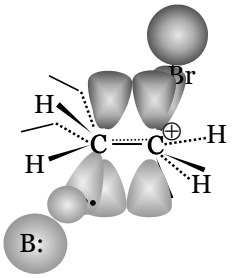
a partial π-bond

LUMO **HOMO**



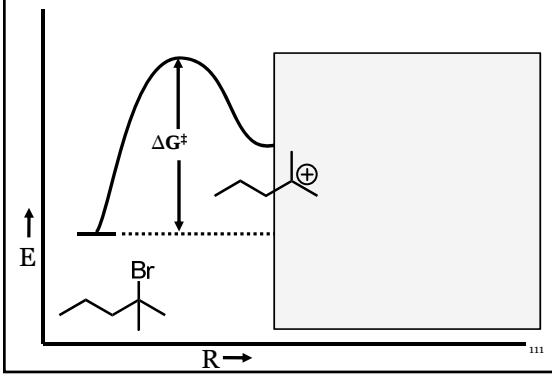
109

Elimination: E1



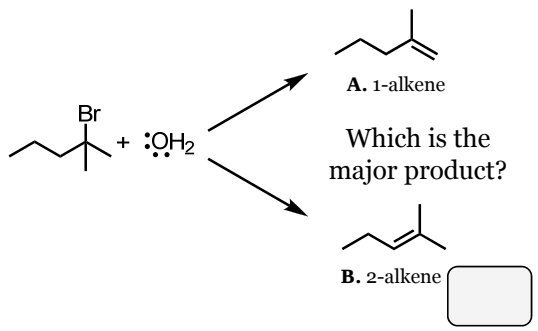
110

Elimination: E1



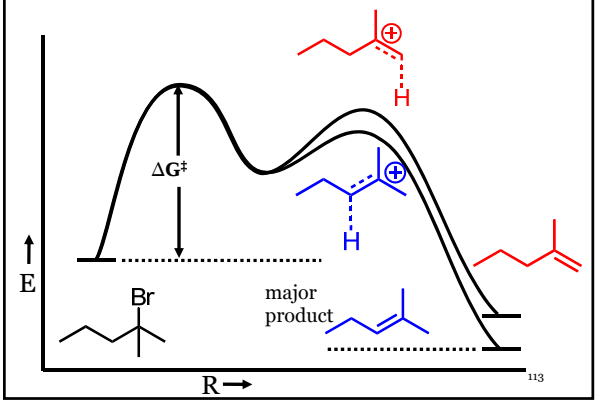
111

Elimination: E1



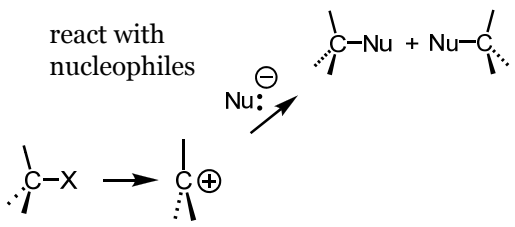
112

Elimination: E1



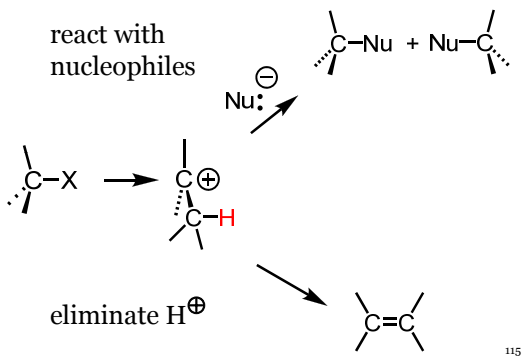
113

Reactions of Carbocations



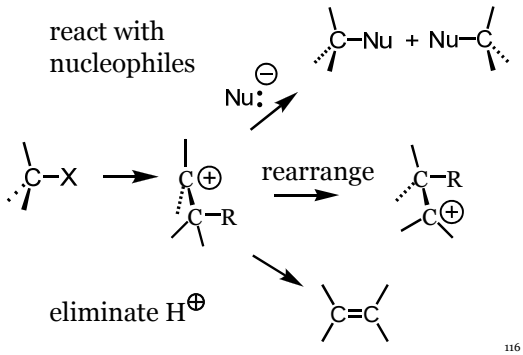
114

Reactions of Carbocations



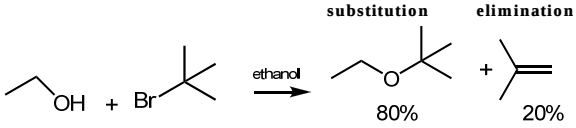
115

Reactions of Carbocations



116

Reaction Mixtures



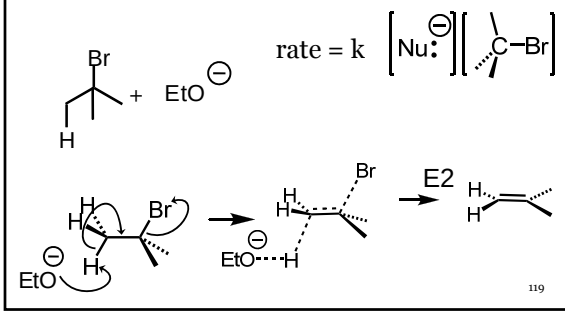
Does increasing the basicity of the nucleophile increase the rate of E1 reaction?

a. Yes b. No

118

Reaction Mechanisms - Kinetics

E2 = Elimination 2nd Order

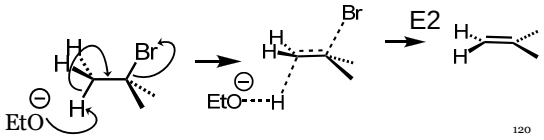


119

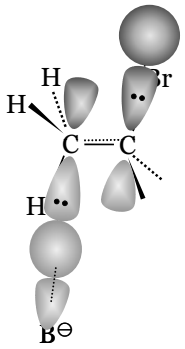
E2 Mechanism

The E2 elimination is *concerted*:

Bond *breaking*
occurs at the same time as
bond *formation*



120

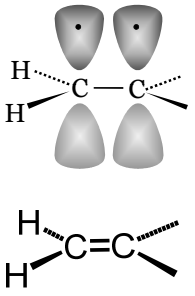


121

concerted reaction => stereoelectronic requirements

C-H and C-Br bonds must lie in the same plane

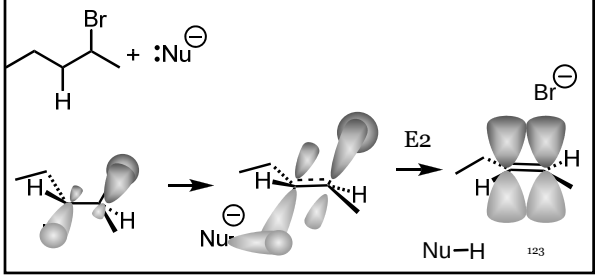
to form the π-bond



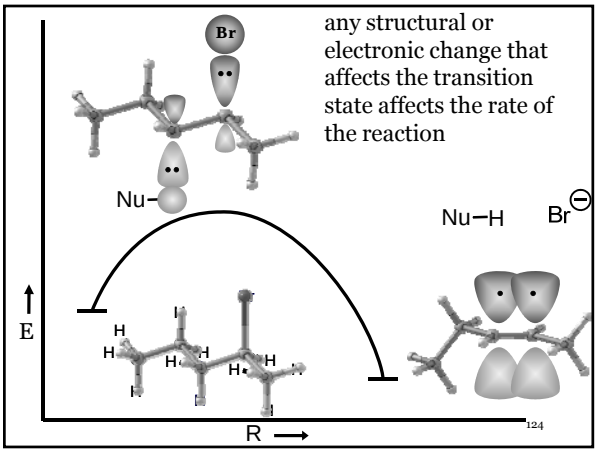
122

concerted reaction => stereoelectronic requirements

C-H and C-Br bonds must lie in the same plane
(*antiperiplanar*) to form the π-bond

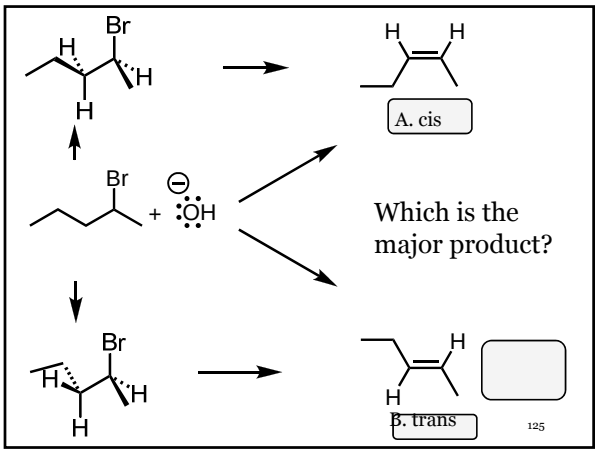


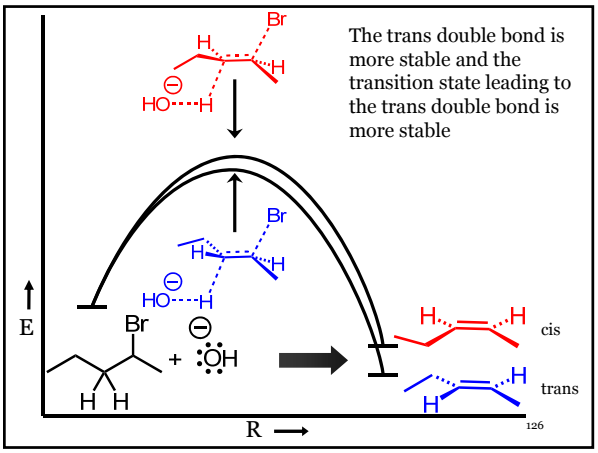
123

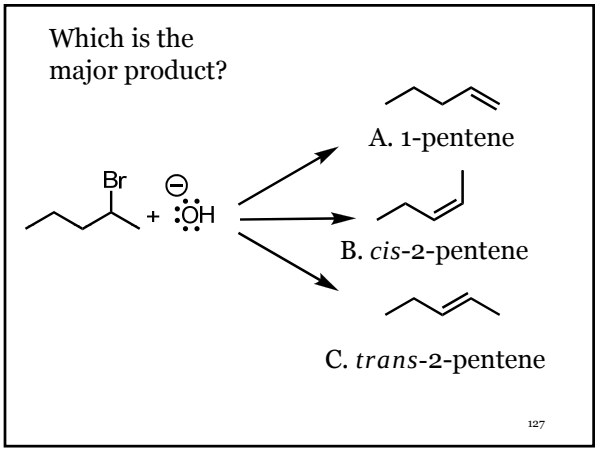


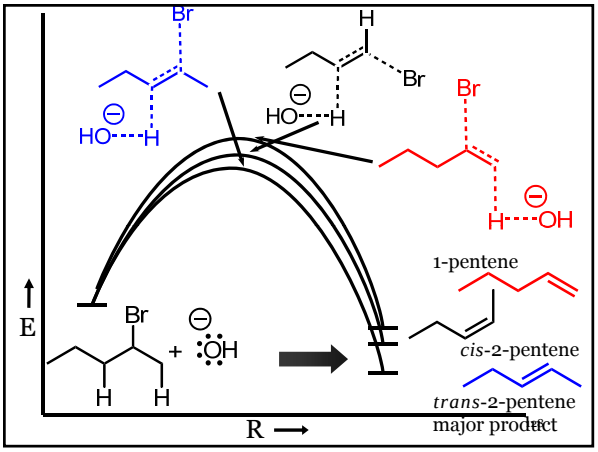
any structural or electronic change that affects the transition state affects the rate of the reaction

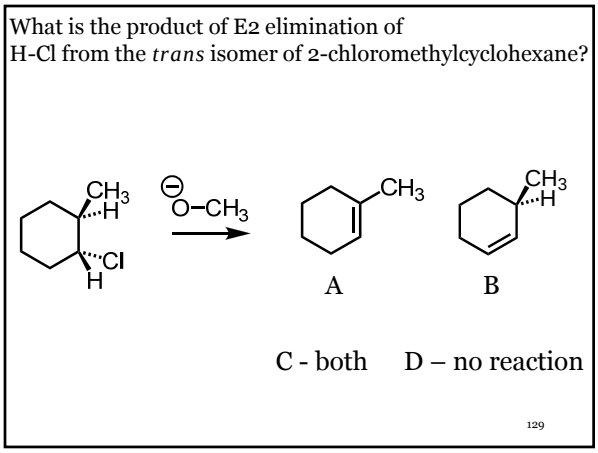
124

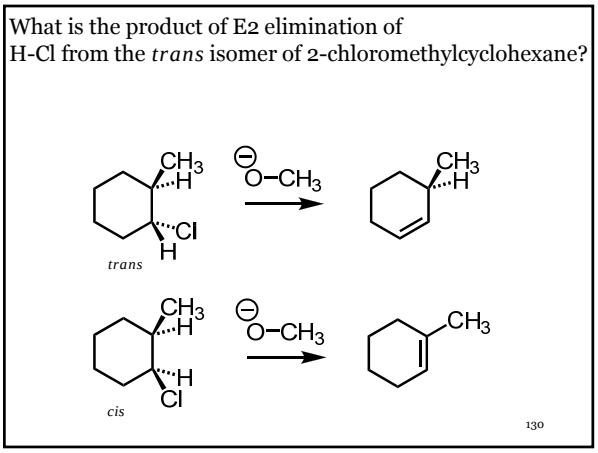

A. cis
Which is the major product?
B. trans
125

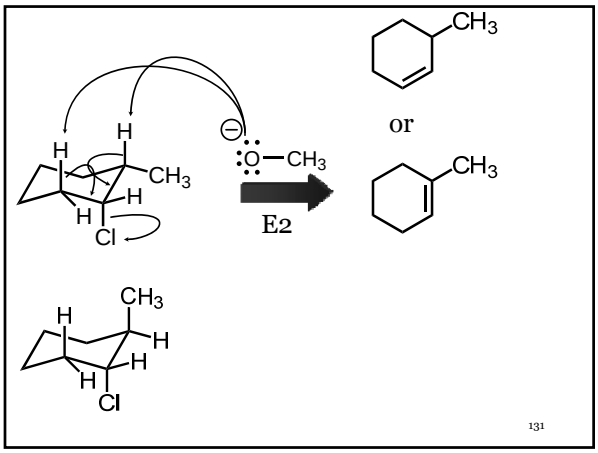

The trans double bond is more stable and the transition state leading to the trans double bond is more stable
E
R
cis
trans
126

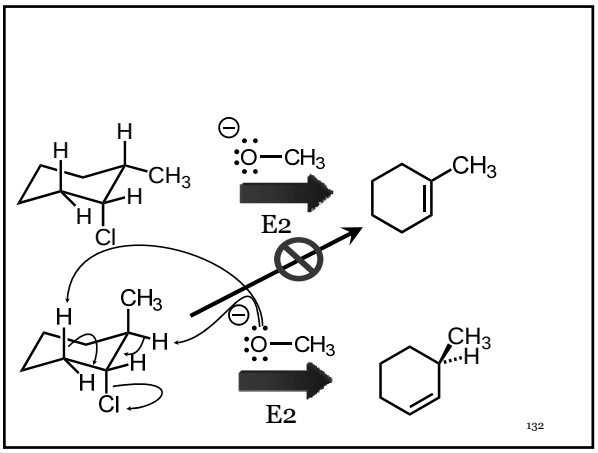

Which is the major product?
A. 1-pentene
B. cis-2-pentene
C. trans-2-pentene
127

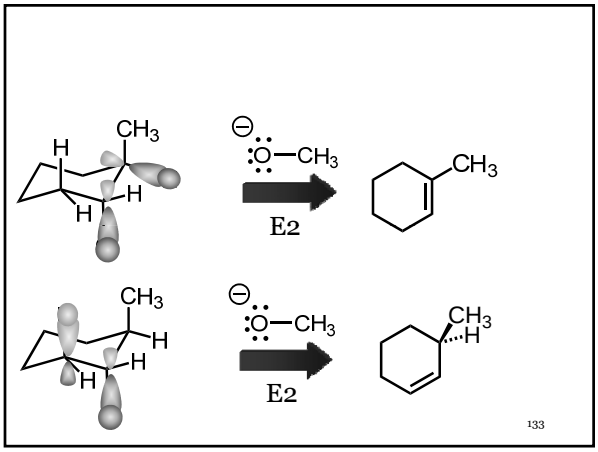

E
R
1-pentene
cis-2-pentene
trans-2-pentene
major product

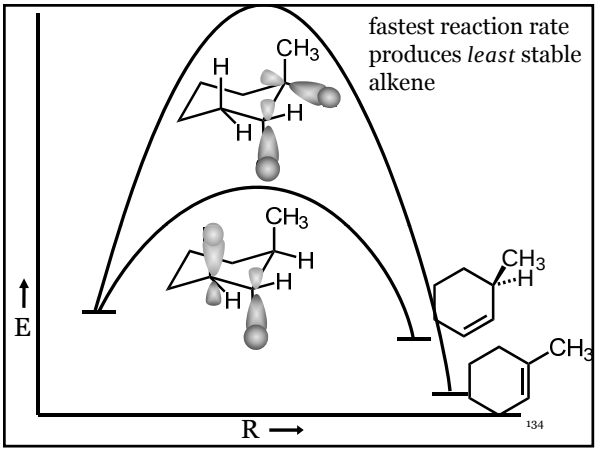

What is the product of E2 elimination of H-Cl from the trans isomer of 2-chloromethylcyclohexane?
A
B
C - both
D – no reaction
129

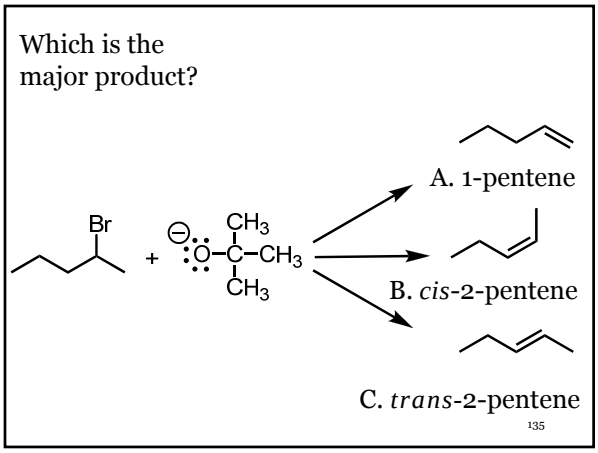

What is the product of E2 elimination of H-Cl from the trans isomer of 2-chloromethylcyclohexane?
trans
cis
130

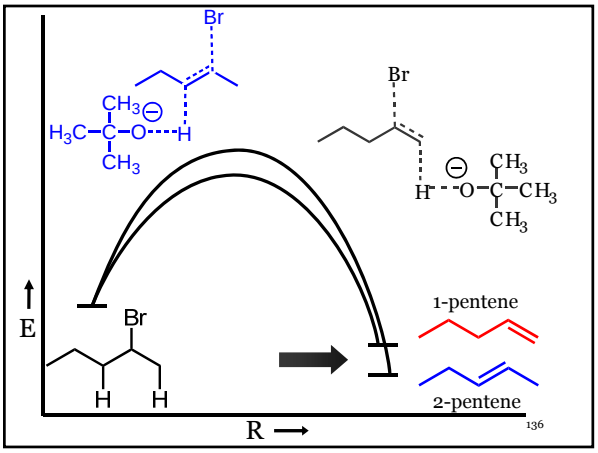

CH3
or
CH3
E2
CH3
Cl
131


CH3
E2
CH3
E2
CH3
Cl
132


CH3
E2
CH3
E2
133


fastest reaction rate
produces *least* stable
alkene
CH3
CH3
CH3
CH3
E
R
134


Which is the
major product?
Br
CH3
CH3
A. 1-pentene
B. *cis*-2-pentene
C. *trans*-2-pentene
135

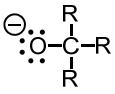

Br
CH3
CH3
Br
CH3
CH3
E
Br
1-pentene
2-pentene
R
136

Steric effects vs electronic effects
Transition state stability

small bases:

steric effect < electronic effect

stability of the double bond

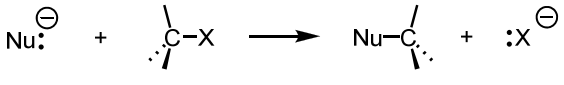


large bases:

steric effect > electronic effect

least hindered proton.

137



Nucleophilicity of the nucleophile

S_N2

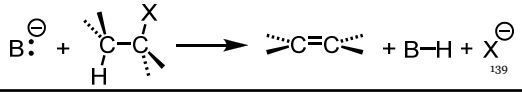
Steric hindrance (nucleophile and substrate)

vs

E2

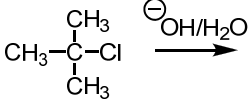
Strength of the base

Steric hindrance (base and substrate)



139

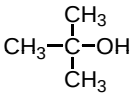
Hindered RCl, strong base



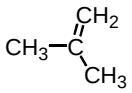
S_N2

vs

E2



I.

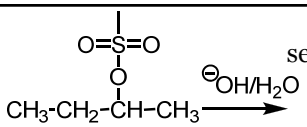


II.

Which is(are) the major product(s)?

A. I. B. II. C. I and II

142

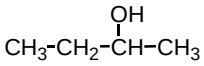


secondary, strong base elimination predominates

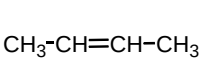
S_N2

vs

E2



I.

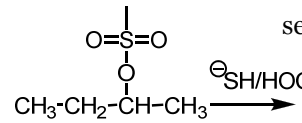


II.

Which is(are) the major product(s)?

A. I. B. II. C. I and II

144

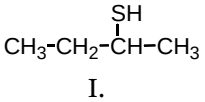


secondary, weakly basic, good nucleophile substitution predominates

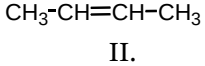
S_N2

vs

E2



I.



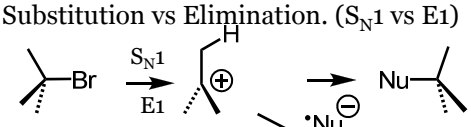
II.

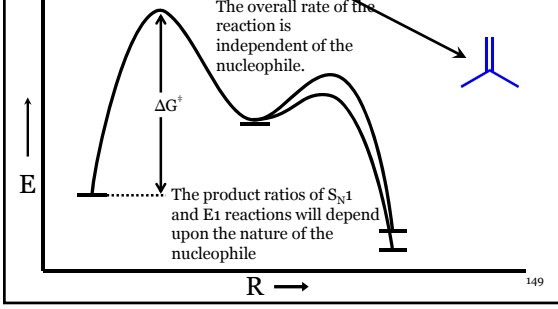
Which is(are) the major product(s)?

A. I. B. II. C. I and II

145

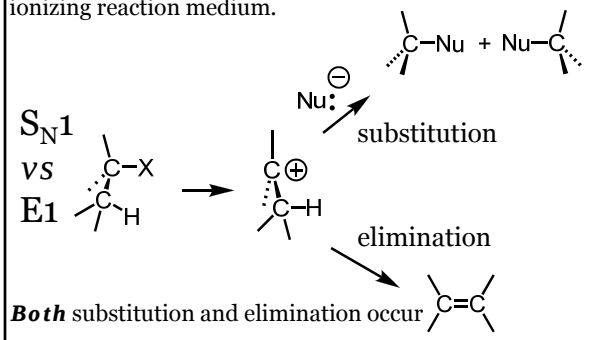
Substitution vs Elimination. (S_N1 vs E1)





149

Both require a stable cation and an ionizing reaction medium.



Both substitution and elimination occur

Elimination favored at high temperature

How can I tell if the reaction is S_N2 or S_N1 or E2 or E1?

Summary of S_N2, S_N1, E2 and E1 reactions.

$CH_3–X$	$R–CH_2–X$	$R–CH(R)–X$	$R–C(R)(R)–X$
	1°	2°	3°
S_N2	mainly S_N2 except with hindered bases eg. $(CH_3)_3CO^-$ when E2 is observed.	mainly S_N2 with weak bases and reactive nucleophiles (I^-, RS^-, CN^-, etc). E2 increases with strong bases. S_N1, E1 in ionizing solvents.	*NO* S_N2. In polar, protic solvents S_N1 and E1 reactions are observed. High temperature favors elimination. When the nucleophile is a strong base, E2 is observed.