(2) **Today**

Chap 11: Reactions of Alkyl Halides: Nucleophilic Substitutions and Eliminations

Sections 11.1 - 11.6: Substitution Reactions

Next Class (3)

Sections 11.1 - 11.6: Substitution Reactions

Sections 10.5, 17.6: Alcohols in Nucleophilic Substitution Reactions

(4) **Second Class from Today**

Sections 10.5, 17.6: Alcohols in Nucleophilic Substitution Reactions

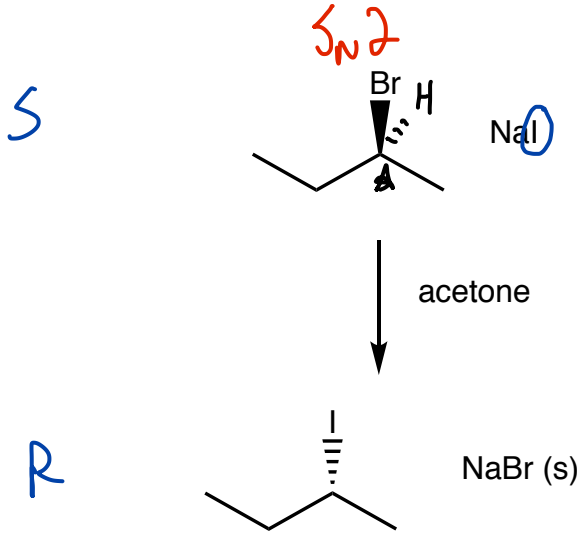
Sections 11:7 - 11:11: Elimination Reactions

Third Class from Today (5)

Sections 11:7 - 11:11: Elimination Reactions

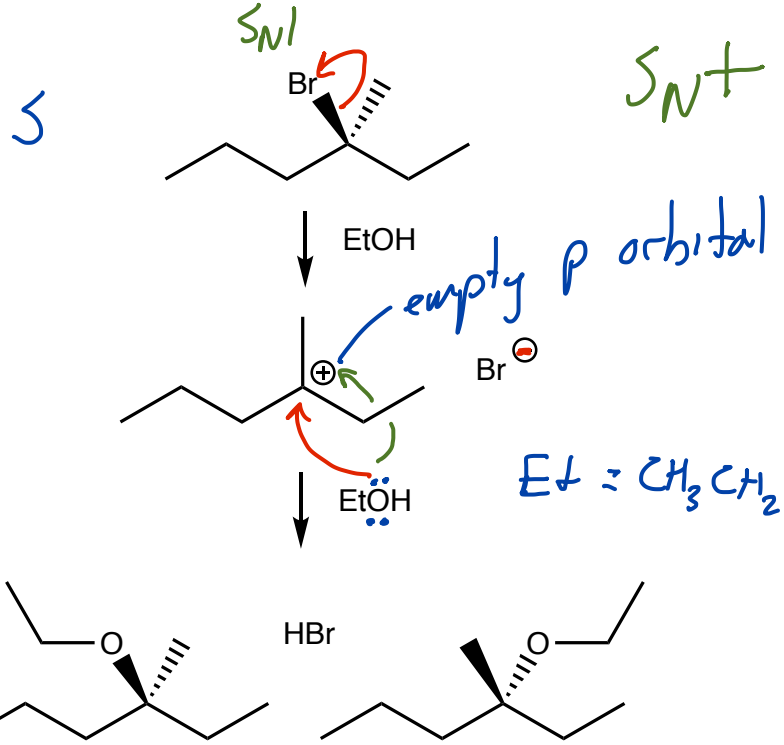
Evidence for S_N2 and S_N1

Section 11.2 and 11.4



The I^- (nucleophile) cannot come in from the side the Br (leaving group) is on.

I^- (nucleophile) comes in from behind, and the stereochemistry is <u>inverted</u> ... only 1 stereoisomer produced.

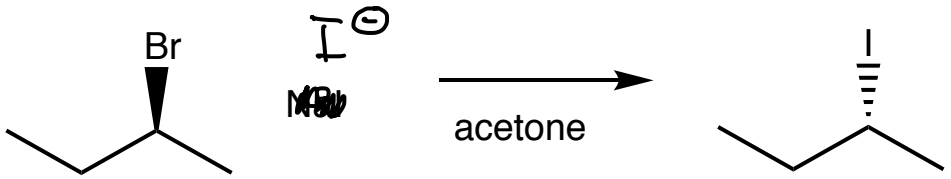


Since a 2^+ forms, the nucleophile can add to both sides, so 2 stereoisomers form

Evidence for S_N2 and S_N1

rate = k [2-bromobutane]^x [$I^\ominus$]^y

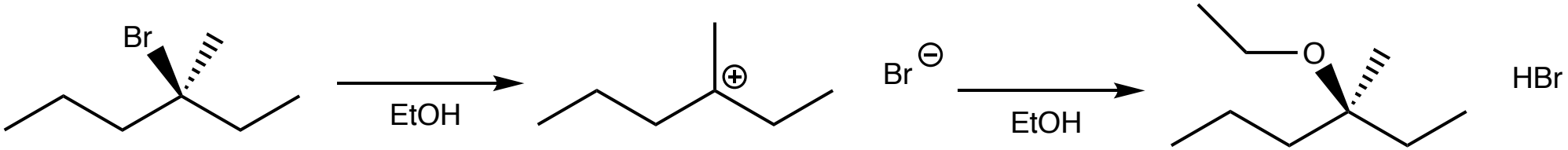
Section 11.2 and 11.4



predicted rate law rate = k [$CH_3CH_2CH_2CH_2Br$][I^-]

rate is positive for the production of product

When S_N2 reactions occur the rate depends on / is proportional to the concentration of the substrate and the nucleophile

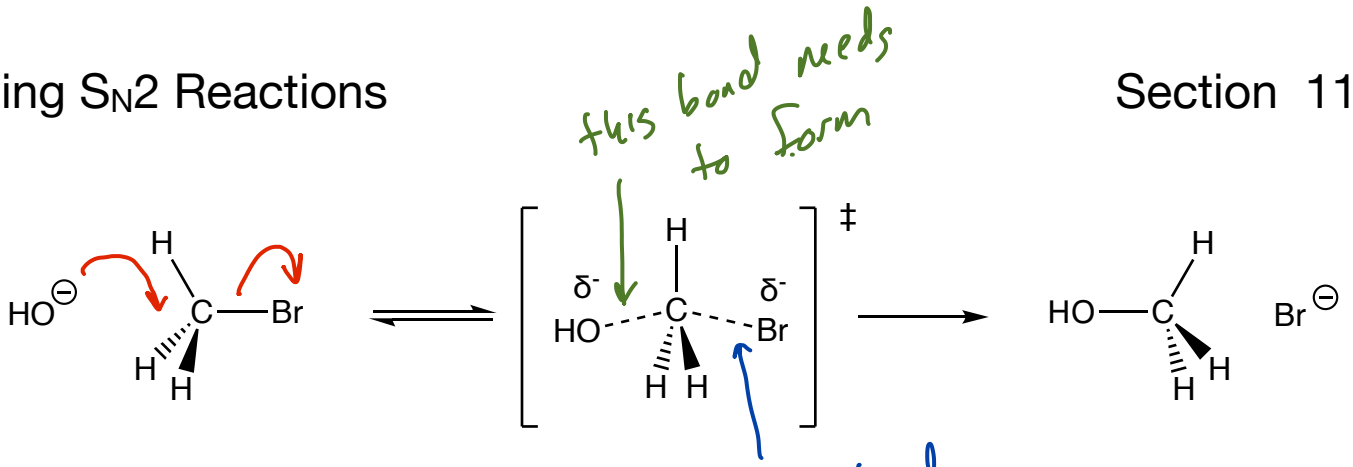


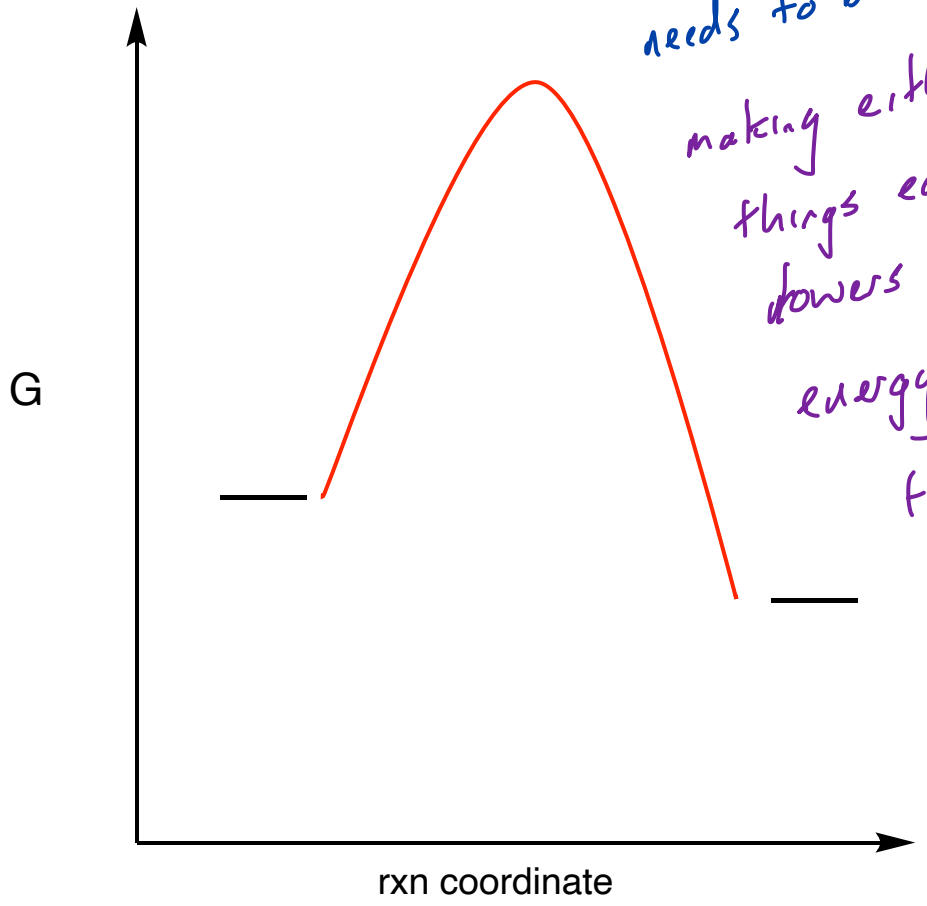
predicted rate law rate = k [$CH_3CH_2CH_2C(CH_3)BrCH_3$]

When S_N1 reactions occur, the rate does <u>not</u> depend on the concentration of the nucleophile

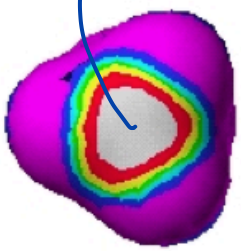
Factors Affecting S_N2 Reactions

Section 11.2 and 11.3

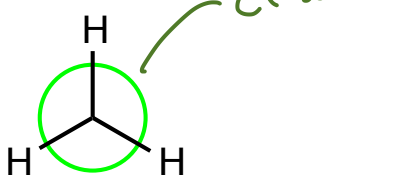




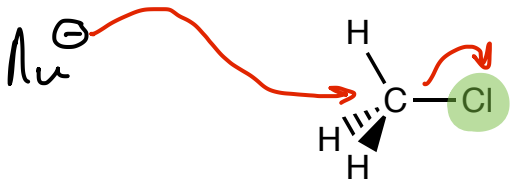
making either of these things easier (making or breaking) lowers the activation energy ($\Delta G^{\ddagger}$) and allows the reaction to occur more quickly

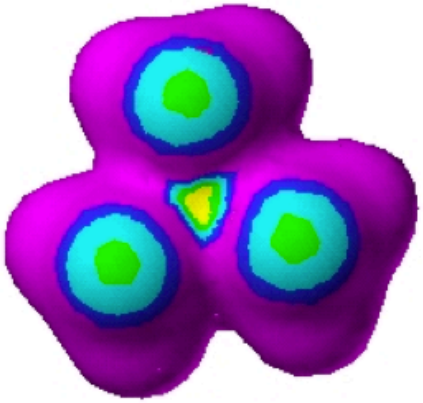


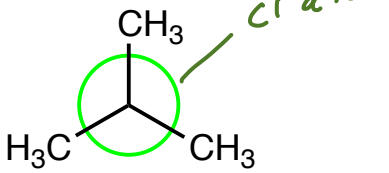
gigantic bullseye



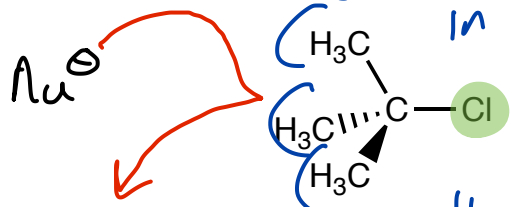
nothing in the way







organic shrubbery in the way



Nu cannot get to the backside of the α-C

access to the backside of the α-C is very important!

S_N2 great

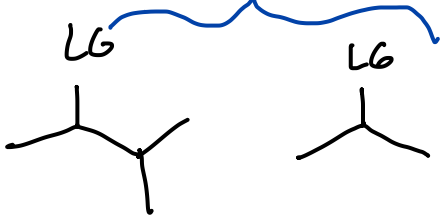
CH_3-LG

methyl α-C

S_N2 fine

1° α-C

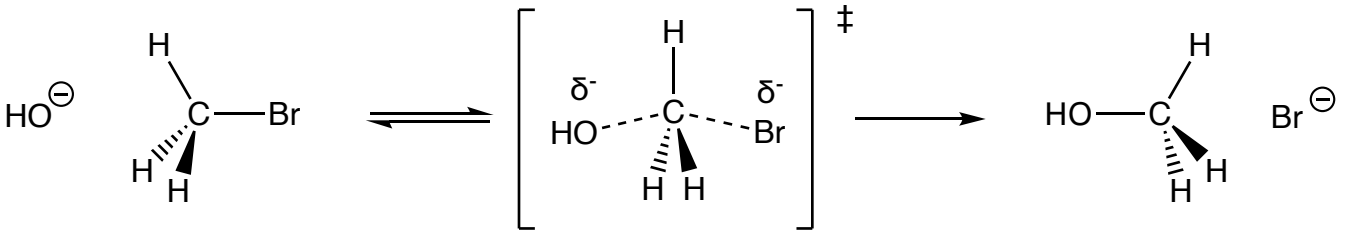
S_N2 meh



2° α-C

~~S_N2~~ nope

3° α-C

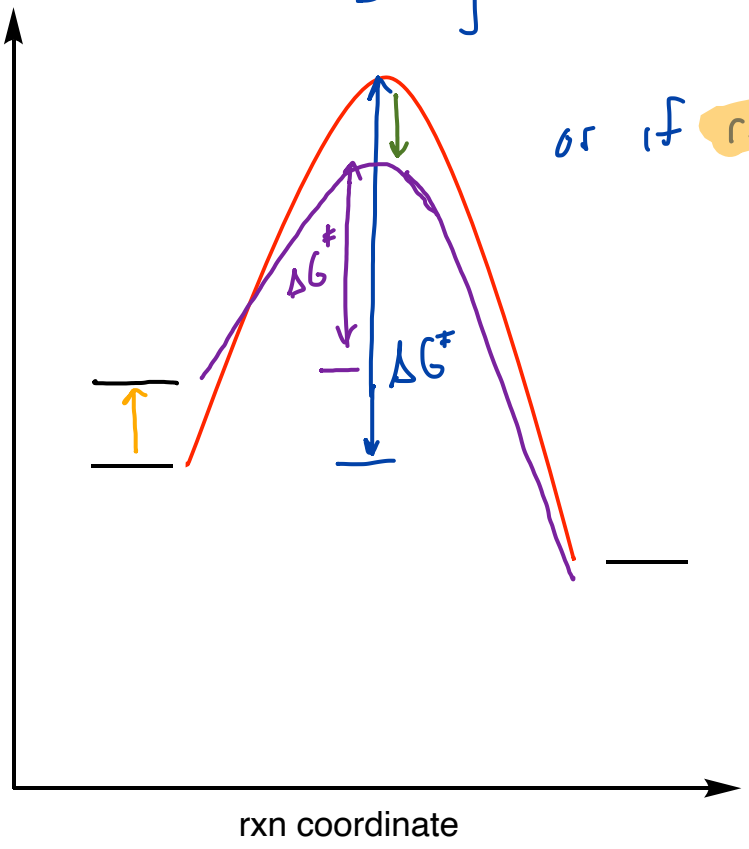


rate = k [$CH_3CH_2CH_2CH_2Br$][Nu^-]

$\Delta G^{\ddagger}$ goes down if TS is stabilized

or if reactants are destabilized

More reactive nucleophiles will raise the energy of the reactants and make the gap between the TS + reactants smaller



increase e^- density increase nucleophilicity

increase size of atom increase nucleophilicity

Factors affecting S_N2: Nucleophile Quality

$Nu:^- + CH_3Br \rightarrow CH_3Nu + Br^-$

Nucleophile		Product		Relative rate of reaction
Formula	Name	Formula	Name	
H_2O:	Water	$CH_3OH_2^+$	Methylhydronium ion	1
$CH_3CO_2^-$	Acetate	$CH_3CO_2CH_3$	Methyl acetate	500
NH_3	Ammonia	$CH_3NH_3^+$	Methylammonium ion	700
Cl^-	Chloride	CH_3Cl	Chloromethane	1,000
$HO:^-$	Hydroxide	CH_3OH	Methanol	10,000
CH_3O^-	Methoxide	CH_3OCH_3	Dimethyl ether	25,000
I^-	Iodide	CH_3I	Iodomethane	100,000
^-CN	Cyanide	CH_3CN	Acetonitrile	125,000
HS^-	Hydrosulfide	CH_3SH	Methanethiol	125,000

stronger base than a water molecule higher in E in H_2O than

strong base high in E very reactive

large polarizable ions/atoms are good nucleophiles

General trend ... stronger base = stronger nucleophile

But weak bases can be good nucleophiles

$HI, HBr, HCl + H_2O \rightarrow H_3O^{\oplus} + I^-, Br^-, Cl^-$