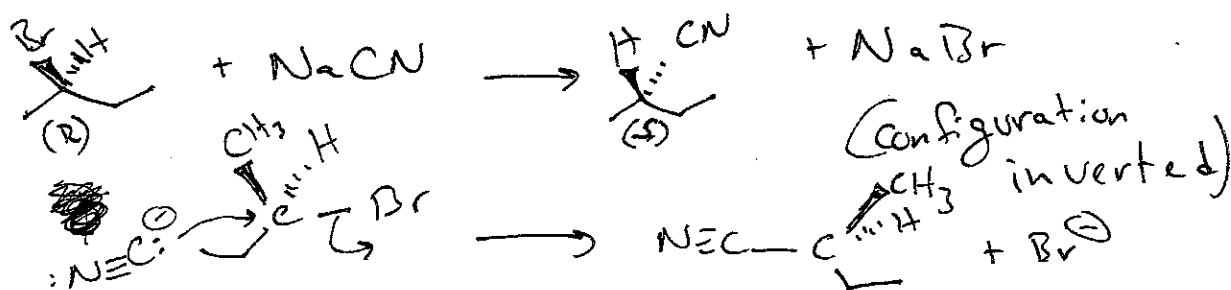


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Last Lecture: Substitution & Elimination Rxns

- 2nd order mechanism
- SN2 reaction
- Stereochemical analysis

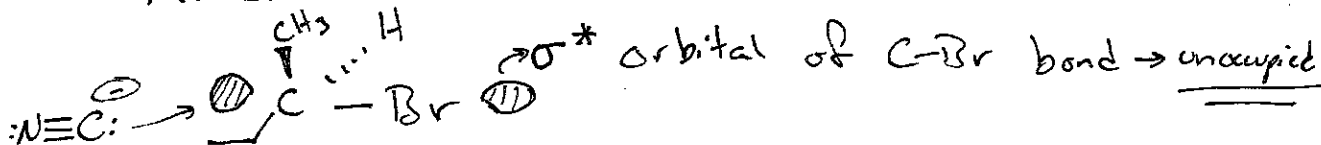


Previously in bromonium ion rxn w/ Br^-
 $\text{C=C} + \text{Br}_2 \rightarrow$ same type of backside attack

Mechanism/Selectivity considerations

1.) Sterics argument (Br takes up room on one side)

2.) M.O.



Nucleophile needs to ~~break~~ attack the unoccupied orbital

C-Br bond breaks due to the nucleophilic e^-

filling the σ^* orbital

C-Br bond weakened by the ~~σ*~~ σ^* having e^- added

New C-C bond forms, while the C-Br bond is breaking

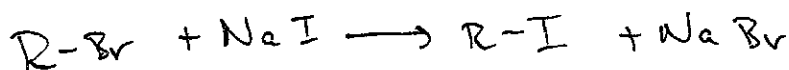
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This is only possible via backside attack!

Factors that influence S_N2 reactivity

- Structure of the electrophile (alpha halide)
 $1^\circ, 2^\circ, 3^\circ$ carbon \rightarrow steric effects
 - Nucleophile reactivity
 - Solvent (solvation of nucleophile)
 - Leaving Group (e.g. Br^-)
- } Strongly Connected

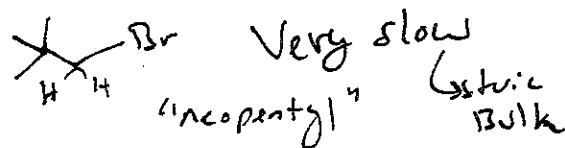
1) Alkyl halide structure \rightarrow (Table 9.3)



SM.	reaction rate
1 ^o CH_3Br	145
1 ^o CH_3CH_2Br	1.0
1 ^o $CH_3CH_2CH_2Br$	0.8
2 ^o $\begin{array}{c} H \\ \\ H-C-CH_2-Br \\ \\ H \end{array}$	0.008
3 ^o $\begin{array}{c} CH_3 \\ \\ H-C-Br \\ \\ CH_3 \end{array}$	~ 0

S_N2 :
 Methyl $> 1^\circ > 2^\circ$
 (3^o Do not react)

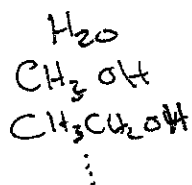
exception of low reactivity:



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2) Nucleophile reactivity & solvent effects

Polar protic solvents



polar aprotic

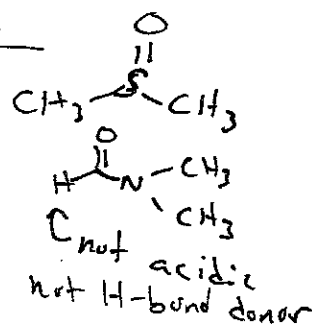
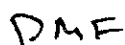


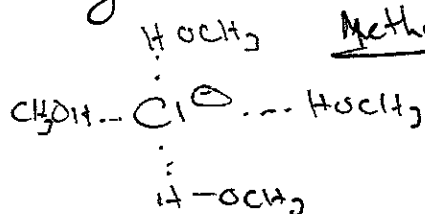
Table 9.6



time needed until rxn is 97% completed

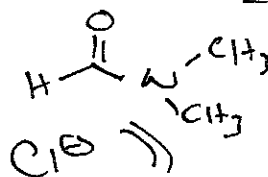
in CH₃OH 13 days } 10⁶ difference
 in DMF 1.4 seconds }

Why do we observe this dramatic difference?



H-bond donors can solvate the Cl⁻ ion

DMF → "Naked" anion



anions are poorly solvated
 no H-bonding

→ More Reactive!

Can ↑ this reactivity
 the cation.

using crown ethers to bind

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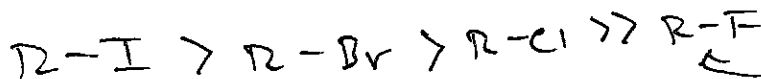
Some notes:

- a) In general, NUC are more reactive in polar aprotic solvents than in polar protic solvents
- b) Intrinsic differences between nucleophiles are larger in the solvents that are less reactive (polar protic)

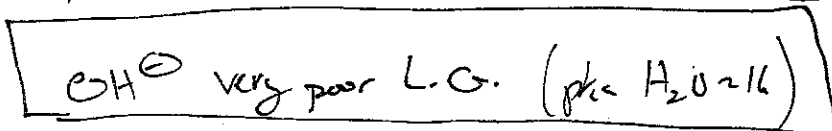
- c) For NUC in the same column of the periodic table, the lower the more reactive



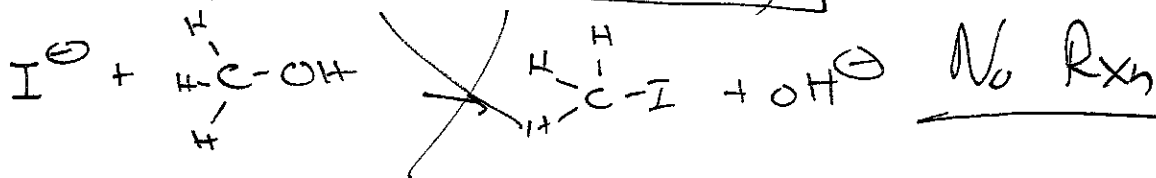
- d) Good Leaving Groups tend to be weak bases (i.e. conjugate base of a strong acid)



← very poor L.G.

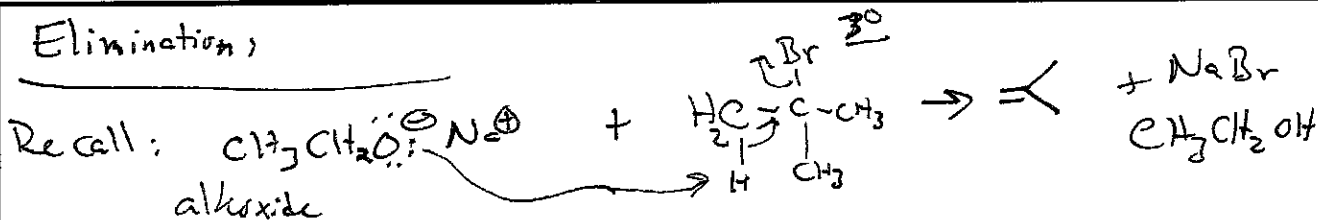


F^- not good L.G.



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Elimination



Kinetic analysis / Rate law

rate = $k [\text{alkoxide}] [\text{alkyl bromide}]$

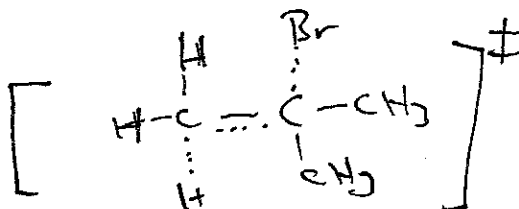
2nd order

(1st order in base, 1st order in alkyl bromide)

E2 rxn

Transition state:

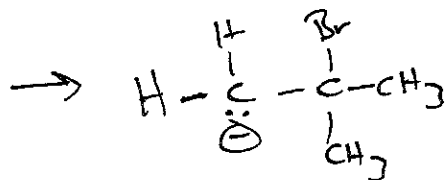
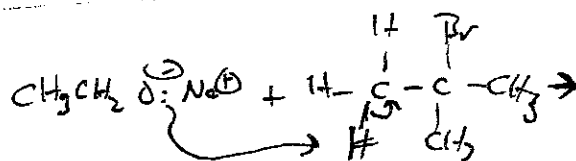
Concerted mechanism



Band breaking

+ Bond forming all together

Alternative (not likely here):



Carbanion

\rightarrow unlikely here, pKa of C-H \approx 50 (vs. $\text{CH}_3\text{CH}_2\text{OH}$ pKa of 16)

No complete deprotonation!

not the right mechanism