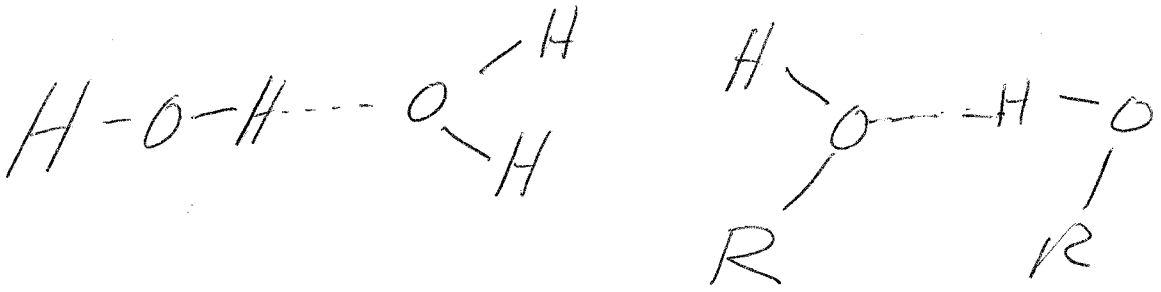
NOTES 12/8/2010

Effect of solvents on SN2/E2/SN1/E1

As noted in last class in Polar protic solvents - nucleophilicity does not parallel basicity as you go down the periodic table

Polar protic solvents are solvents that can hydrogen bond such as water H-O-H or Alcohols H-O-R

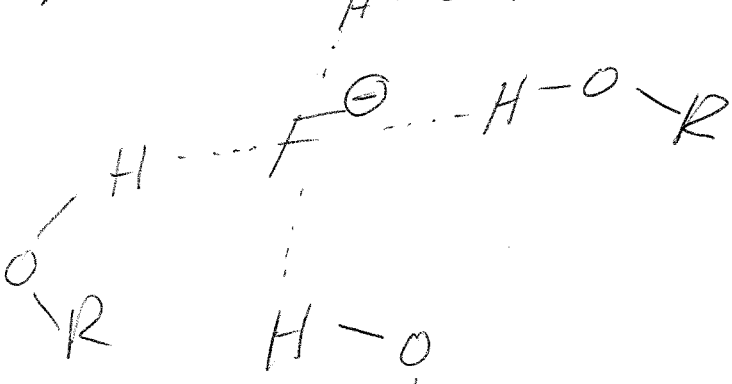


When you consider

F^- vs Cl^- vs Br^- vs I^-

F^- has the largest charge/volume ratio and I^- has the smallest charge/volume ratio

$F^{\ominus}$ being the strongest base
/largest charge/volume or charge/surface
area ratio interacts the
most strongly with protic solvents



So, $F^{\ominus}$ travels through the
Solution dragging a ball of
Solvent. The solvent impedes
the ability of the $F^{\ominus}$ to
attack or be a nucleophile

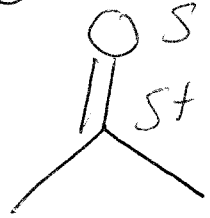
For $I^{\ominus}$ the solvation is
weaker so $I^{\ominus}$ behaves more
like a free nucleophile

3/6

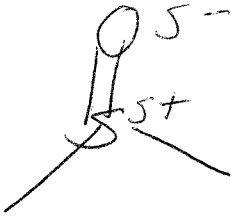
S_N2/E_2 reactions are accelerated by polar aprotic solvents and decelerated by polar protic solvents

Why?

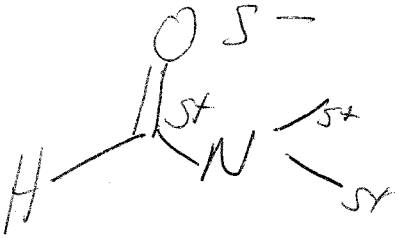
Consider structure of Polar Aprotic solvents e.g.



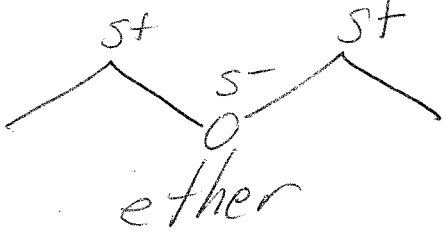
Acetone



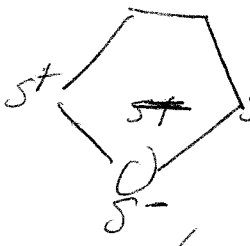
DMSO



DMF



ether



THF

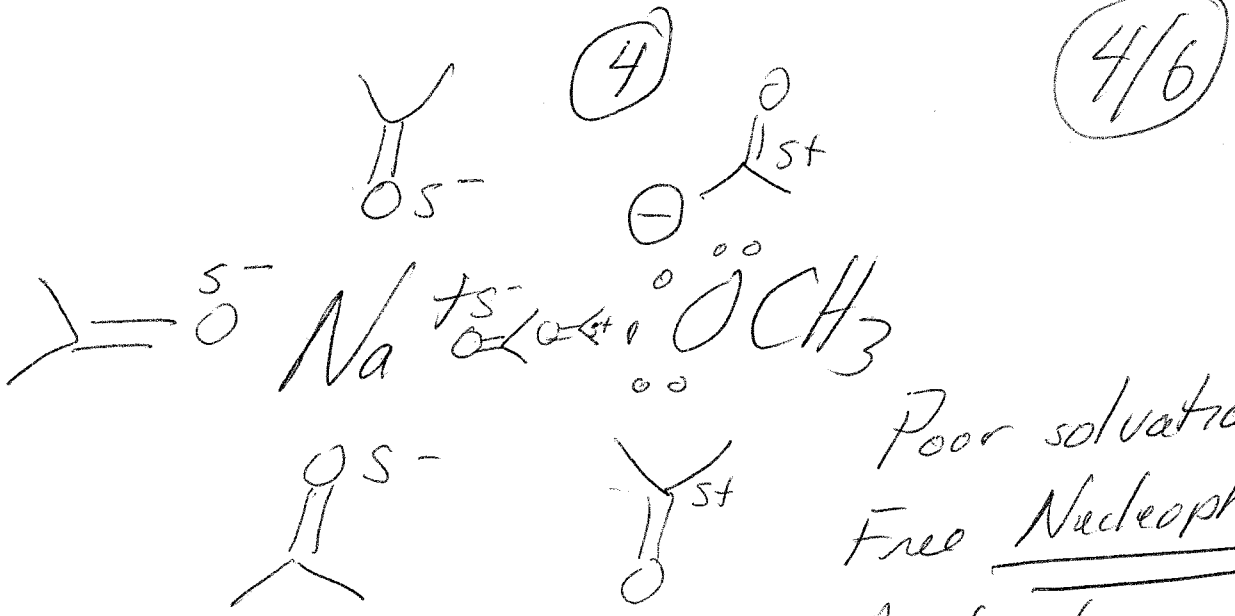
NOTICE δ+ is on internal atom

Not as accessible

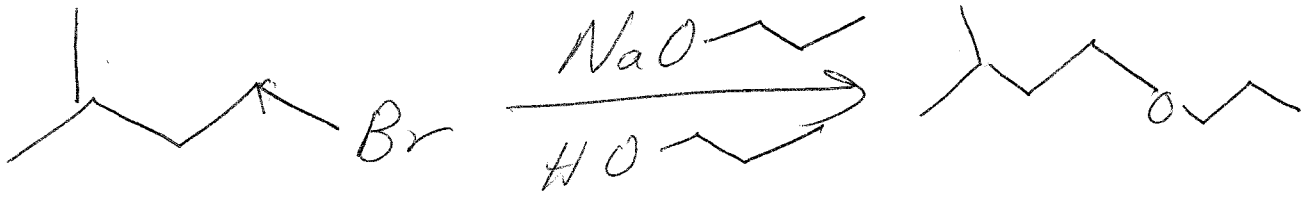
POLAR Aprotic solvents

Solvate CATIONS well Why

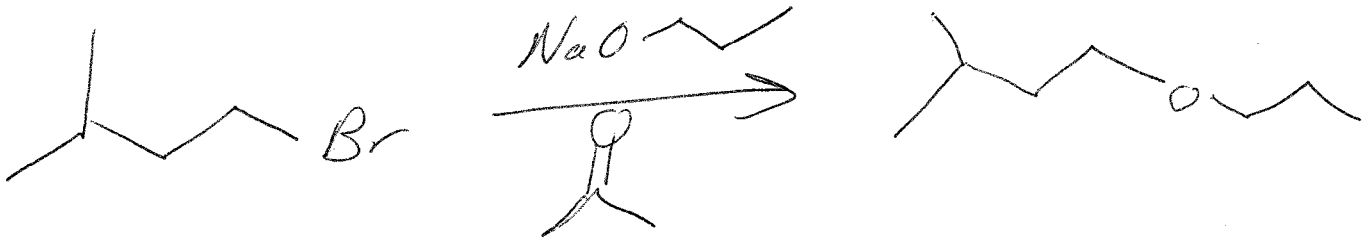
Anions Poorly



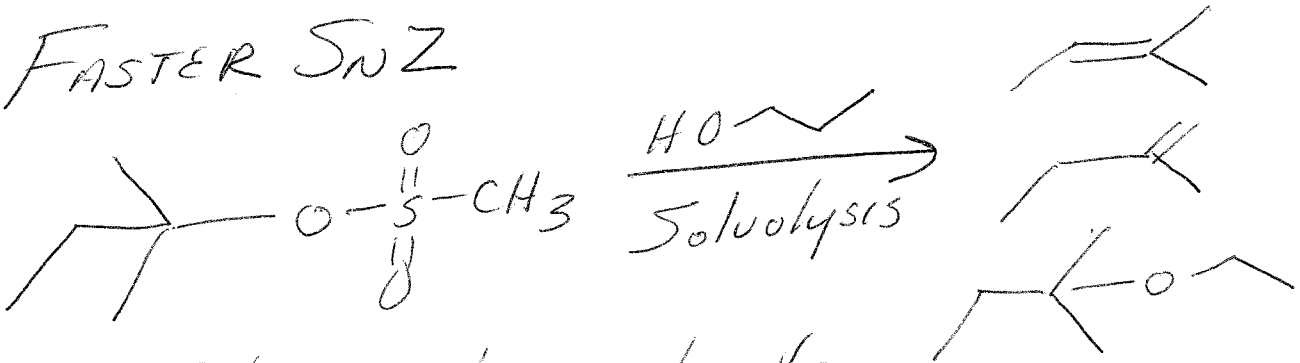
Poor solvation
Free Nucleophile
Accelerates
Attack



Slower SN2



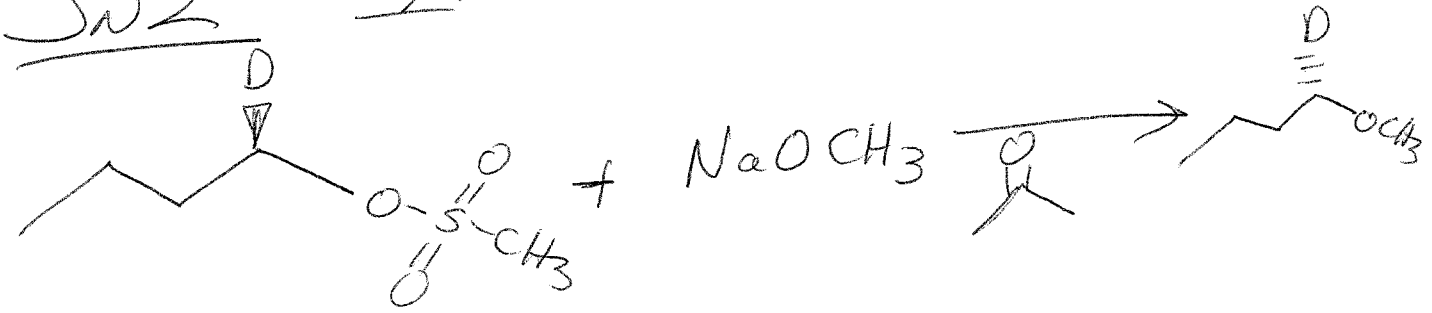
FASTER SN2



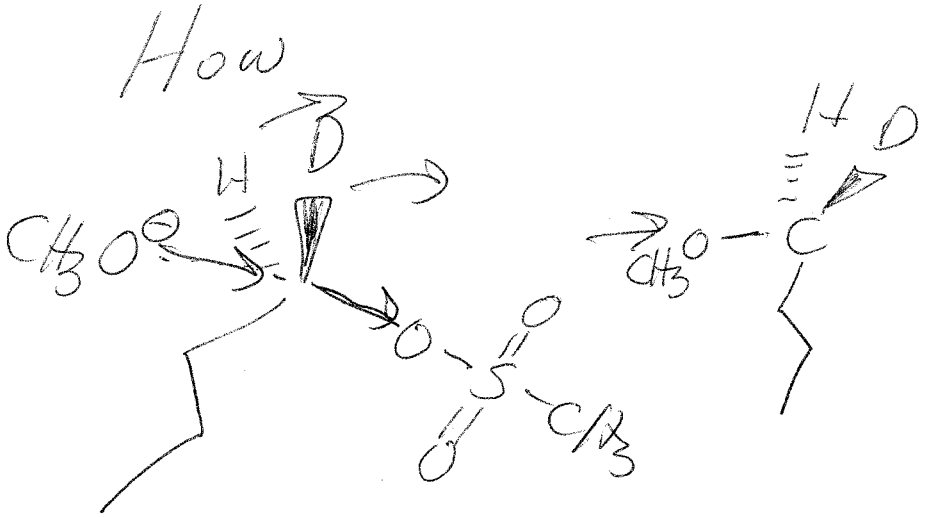
Polar protic solvents
accelerate SN1/E1

Stereochemistry of Rxns

S_N2 – Inversion



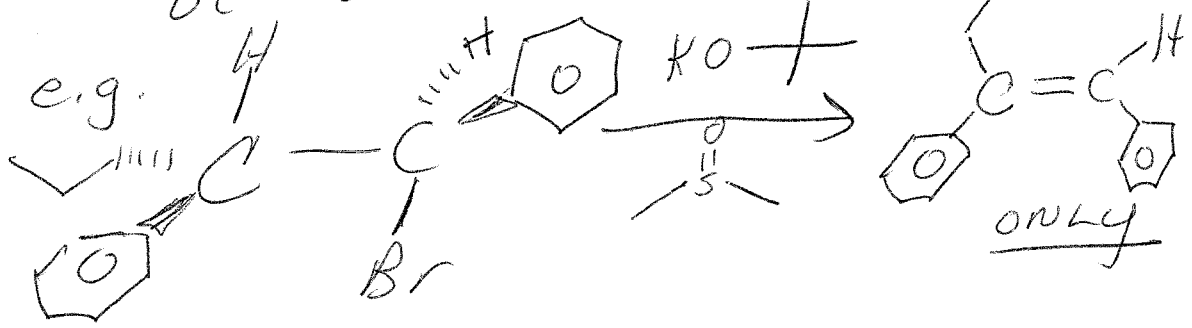
How



E_2 – ANTI elimination

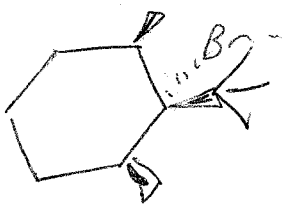
BH and leaving groups must be anti. Must ROTATE

e.g.



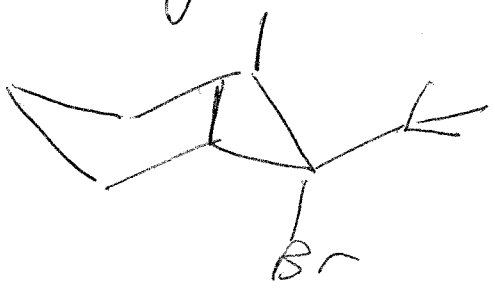
ONLY

6 6/6



No Rxn

Why?



No anti BH

SN1/E1

CATIONS Do 3 things

Eliminate
Substitute (Add)
Rearrangement

SN1 – Get every stereoisomer just like addn.

E1 – Get mostly highly substituted

– Z/E possible