

nucleophilic substitution

1 LEAVING GROUP

READ 9.1-9.8

2 SOLVENT

PROBLEMS 9.1-9.36

3 REARRANGEMENT

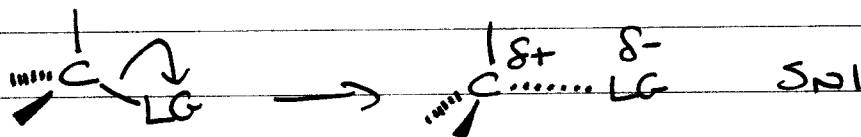
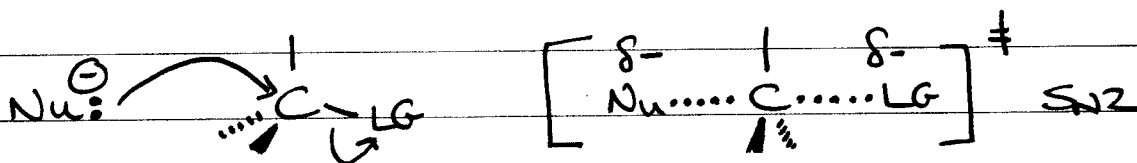
MY OH  
POSTPONED

4 SN SUMMARY

5 NEIGHBORING GROUP PARTICIPATION

6 PHASE TRANSFER CATALYSIS

1 LEAVING GROUP



LG develops -ve charge in TS, so better charge stabilization, lower energy TS, faster RXN.

THUS more acidic H-LG, more stable LG<sup>-</sup>

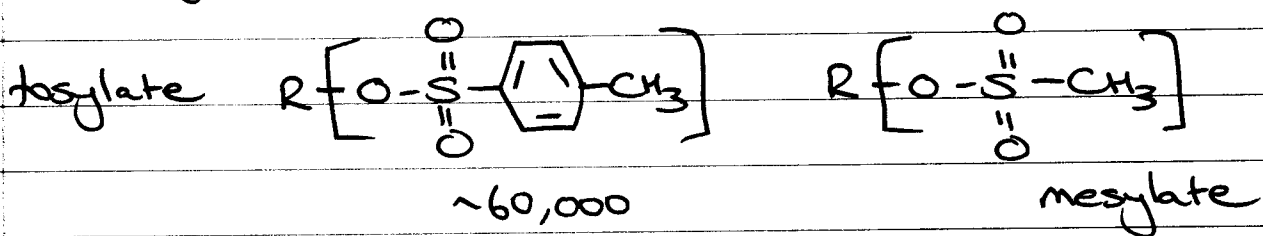
GOOD/BAD LEAVING GROUPS

- relative reactivity

$\text{NH}_2^-$	$\text{OH}^-$	$\text{OR}^-$	$\text{F}^-$	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
⏟						
← 1			1	200	10000	30000

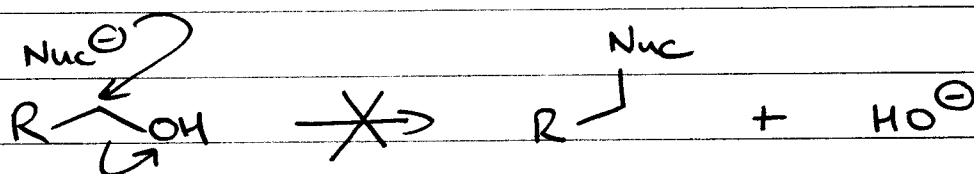
②

other good LG

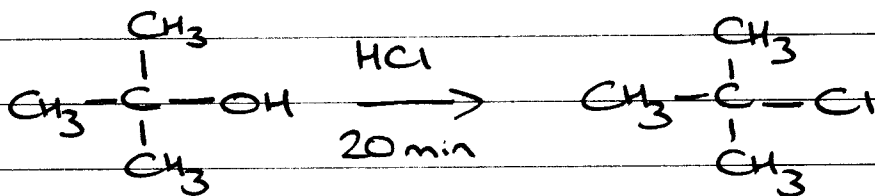


So R-F, R-OH, R-OR', R-NH<sub>2</sub>

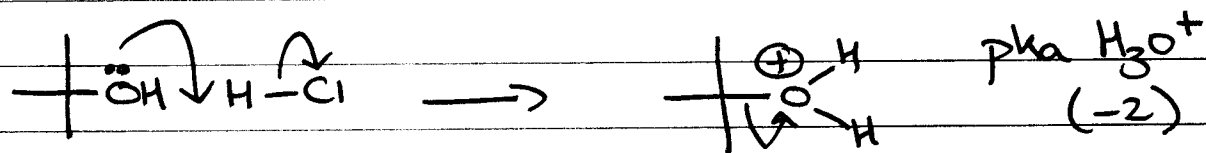
do NOT undergo S<sub>N</sub>2 reactions



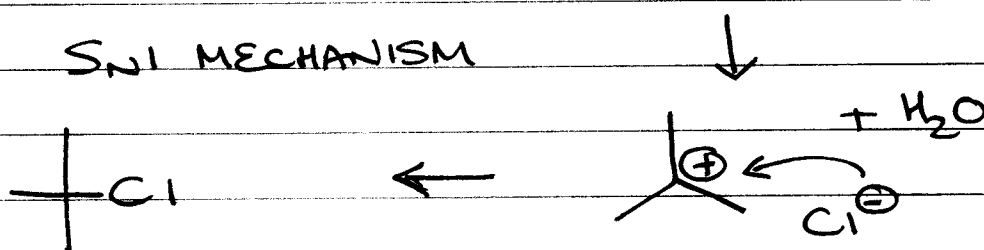
BUT

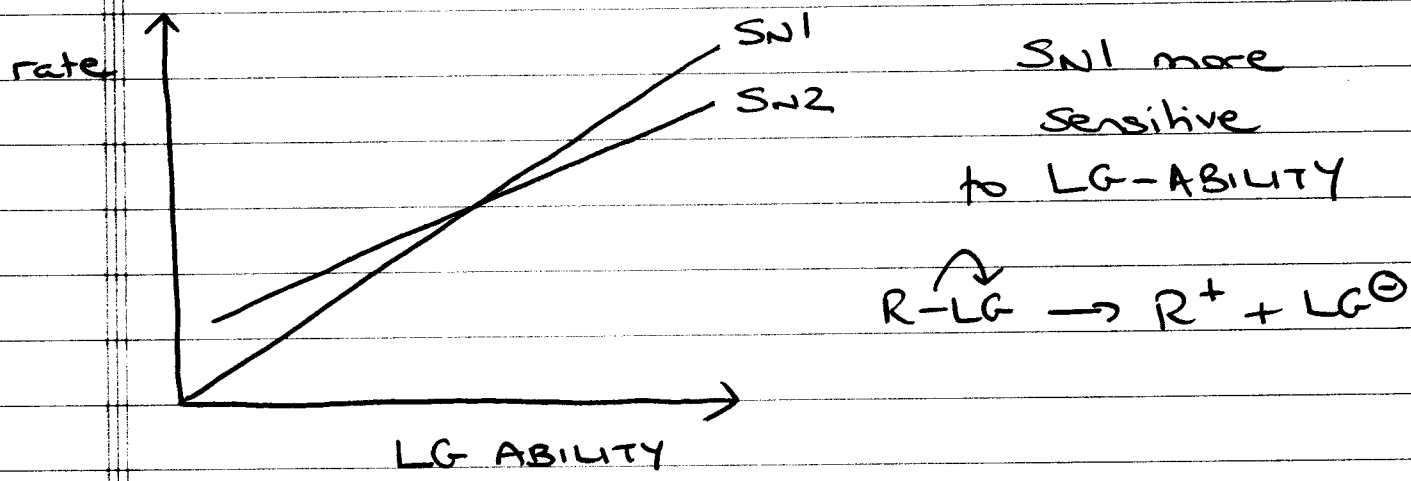


-OH converted into good LG



S<sub>N</sub>1 MECHANISM

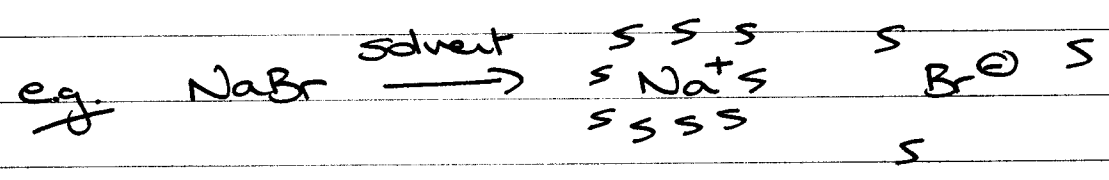




In SN2, as long as LG<sup>⊖</sup> more stable than Nu<sup>⊖</sup>, reaction can proceed BUT LG ABILITY alone cannot determine SN1 vs SN2

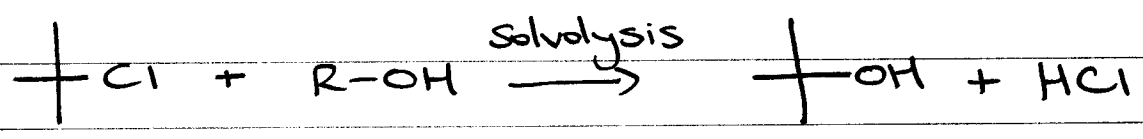
② SOLVENT

- SN2 POLAR APROTIC solvents  
(solvate cations well, but not anions)



- SN1  $R-LG \rightarrow R^{\oplus} + LG^{\ominus}$   
creation & separation of charge

⇒ more POLAR the solvent, the better



Water/ETOH	rel. rate
100 / 0	100,000
80 / 20	14,000
40 / 60	100
0 / 100	1

S<sub>N</sub>2

S<sub>N</sub>2 reactions

DISFAVORED IN PROTIC SOLVENTS

(ground state energy lowered by solvation)

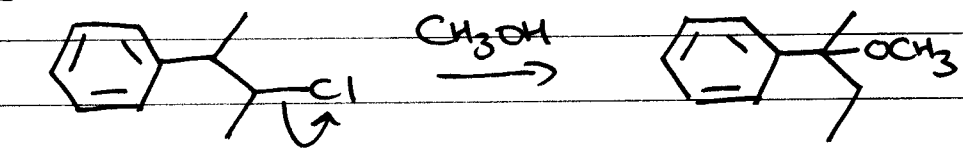
S<sub>N</sub>1 reactions

FAVORED IN PROTIC SOLVENTS

(transition state energy lowered by solvation)

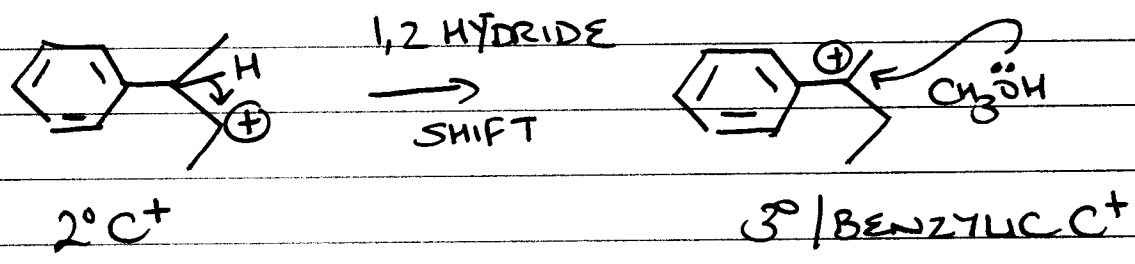
③ REARRANGEMENT (S<sub>N</sub>1/C<sup>+</sup>)

e.g.



↓ S<sub>N</sub>1

↑↑

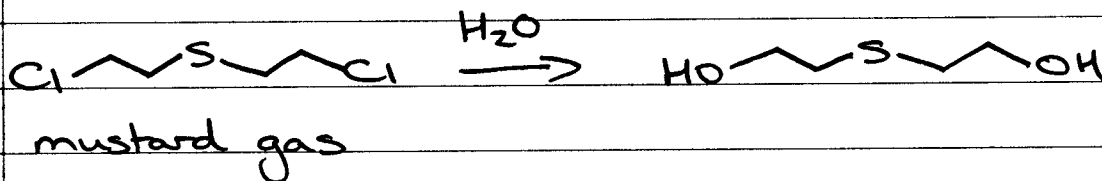


④ S<sub>N</sub> SUMMARY

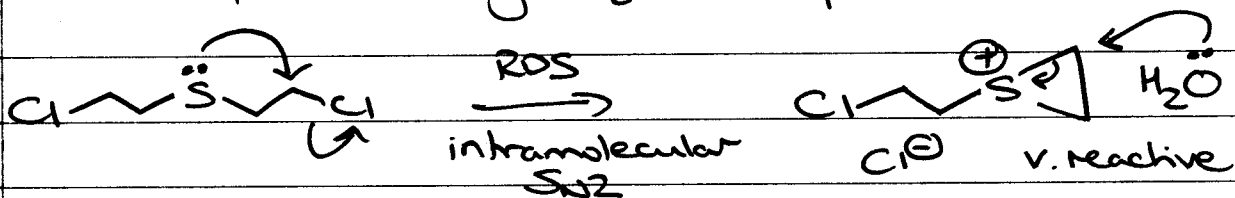
ELECTROPHILE	S <sub>N</sub> 2	S <sub>N</sub> 1
Me/I°	✓	X
2°	GOOD NUC POLAR APROTIC	POOR NUC POLAR PROTIC (GOOD LG)
3°	X	✓

- gets COMPLICATED => elimination

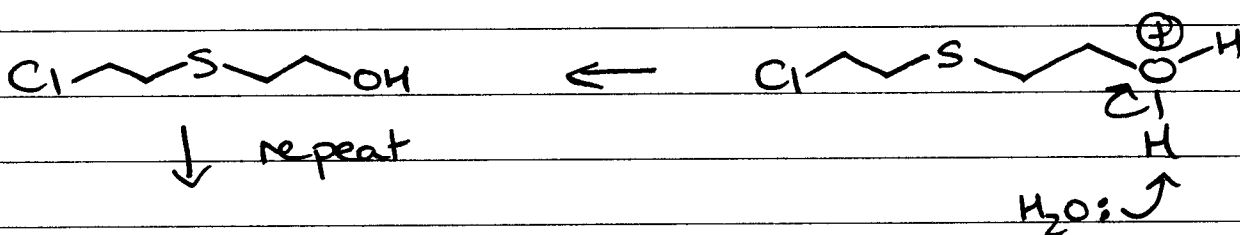
⑤ NEIGHBORING GROUP PARTICIPATION



V. RAPID, even though H<sub>2</sub>O is a poor NUCLEOPHILE



overall rate = k [ClCCSCCCl]  $\downarrow$  Fast S<sub>N</sub>2 rxn

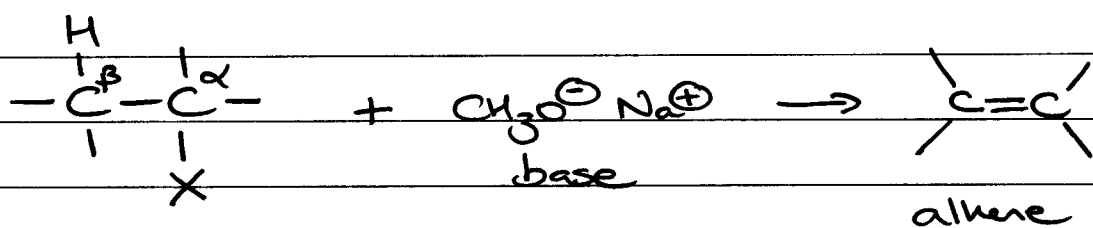


INDEPENDENT of  $[Nuc]$

Two consecutive  $S_N2$  reactions with  $S_N1$  kinetics

⑥ PHASE TRANSFER CATALYSIS  
(read section in the book)

⑦ INTRO TO  $\beta$ -ELIMINATION  
- dehydrohalogenation (one example)

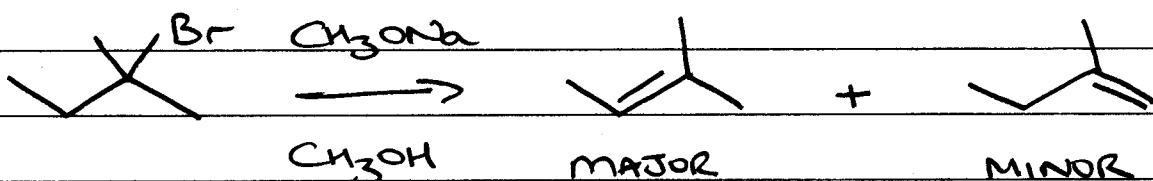
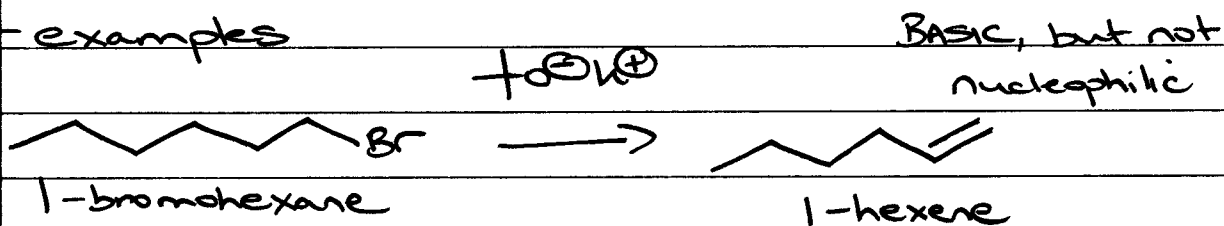


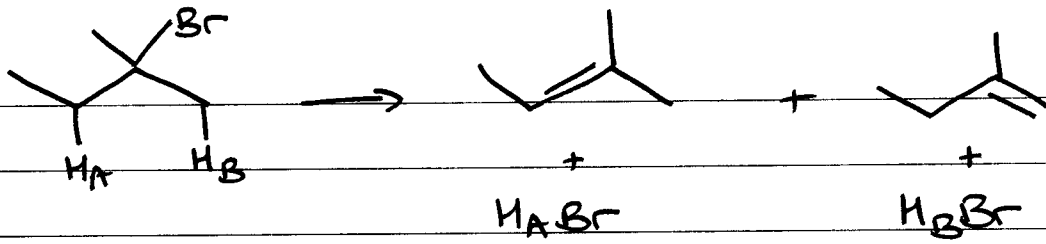
$\beta$ -elimination



ELIMINATION competes w/ SUBSTITUTION

examples





β-PROTONS

ZAITSEV'S RULE → major product is the most substituted alkene (more stable)

... and there are exceptions to this rule