KEY

Chapters 8

Chem 30A- Week 9

Warm-up Exercise

Which pair reacts faster in a S_N2 reaction with a hydroxide ion?

a. CH_3Br or CH_3I — I^- is a better leaving group

b. CH_3CH_2I in EtOH or DMSO — EtOH will hydrogen bond w/ ^-OH & decrease its reactivity

c. H_2CCHBr or H_2CCHBr — because vinylic halides are unreactive to displacement reactions.

Which reagent in the pair is more nucleophilic?

d. BF_3 or F^- — BF_3 is not a nucleophile it is electrophilic

e. $(CH_3)_3P$ or $(CH_3)_3N$ — Nucleophilicity ↓ as down a column

f. H_2O or CH_3COO^- — Nucleophilicity parallels basicity (when comparing nuc. w/ same attacking atom) – more basic = more nucleophilic

BUT be careful of solvent effects!!

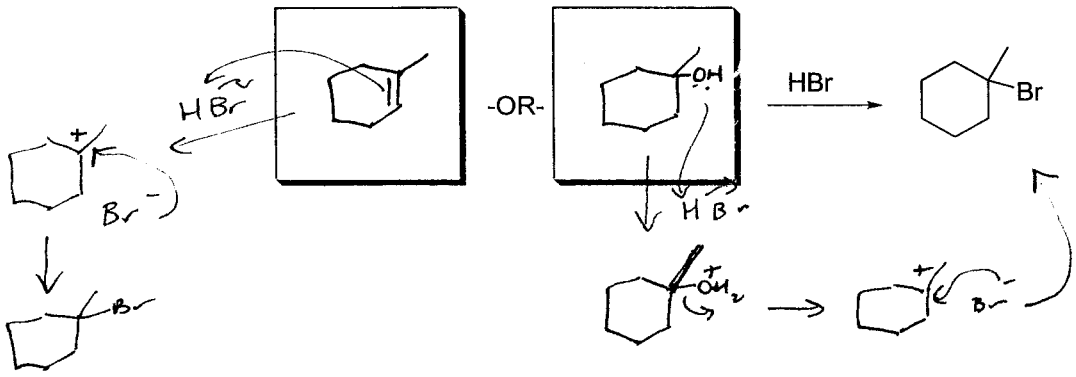
Order each set of compounds with respect to S_N1 reactivity

(S_N1 reactivity depends on LG & C^+ stability)

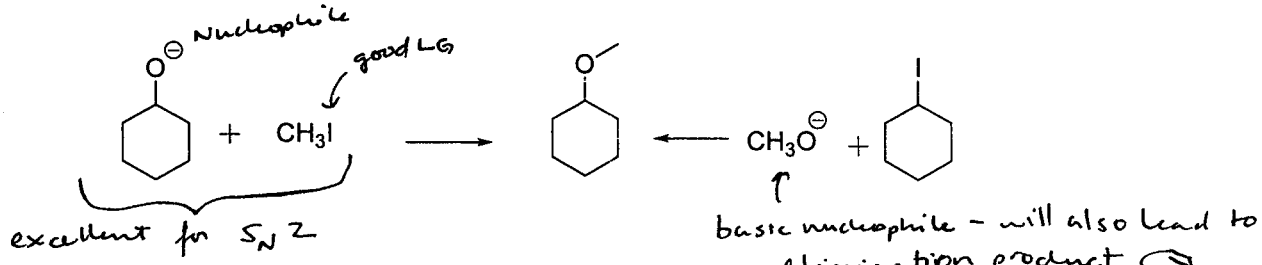
g.	$(CH_3)_3C$-Cl (2)	Ph-$C(CH_3)_2Cl$ (1) (most stable C^+)	$CH_3CH_2C(NH_2)HCH_3$ (3)
h.	$(CH_3)_3C$-F (2)	$(CH_3)_3C$-Br (1) (best LG)	$(CH_3)_3C$-OH (3)
i.	Ph-CH_2Br (3)	$PhCH(CH_3)Br$ (2)	$(Ph)_3CBr$ (1) most stable C^+

Substitution

1. Give two starting materials for the following reaction

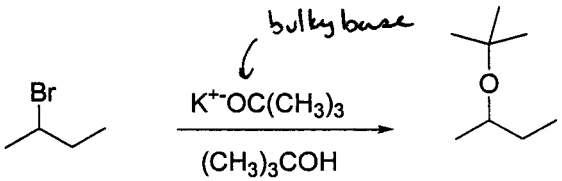


2. Which way would you use to make cyclohexyl methyl ether using a S_N2 reaction?

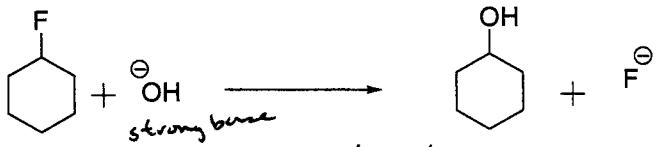


4. The synthetic sequences shown here are all unlikely to occur as written. What is wrong with each?

a.

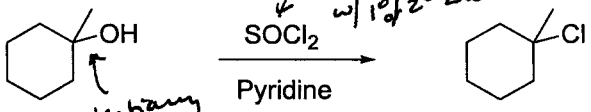


b.



strong base will also lead to elimination product

c.



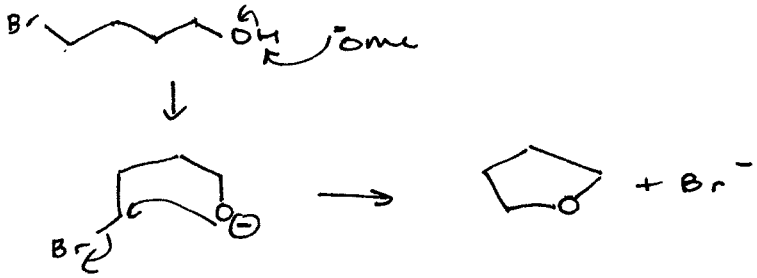
only works w/ 1° or 2° alcohols

tertiary alcohol

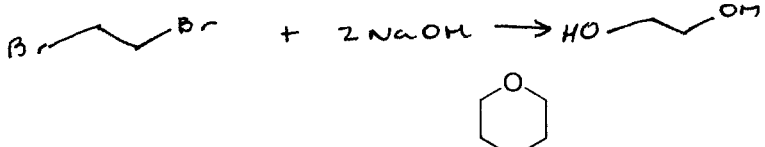
S_N2 will not occur — instead E_2 elimination

there are switched on your worksheet

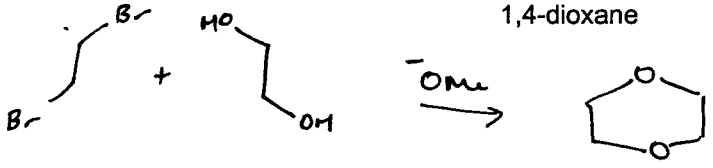
3. What is the product of the intramolecular S_N2 reaction of 4-bromo-butanol with sodium methoxide (base)?



b. Given the above reaction: how would you make 1,4-dioxane from a di-halide starting material?



1,4-dioxane

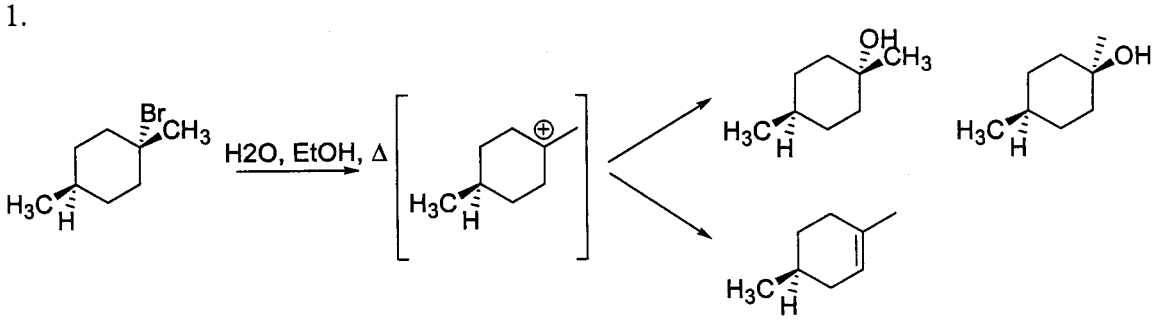


same mech as above

Chem 30A- Week 9 key

Substitution vs. Elimination

1.



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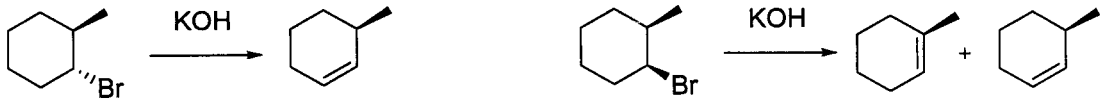

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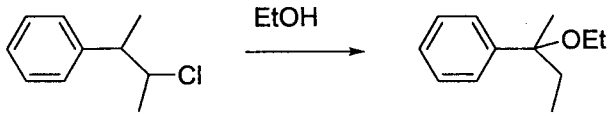

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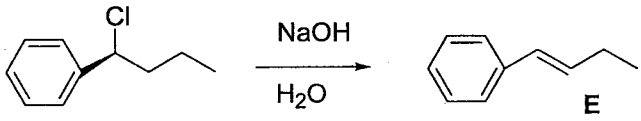

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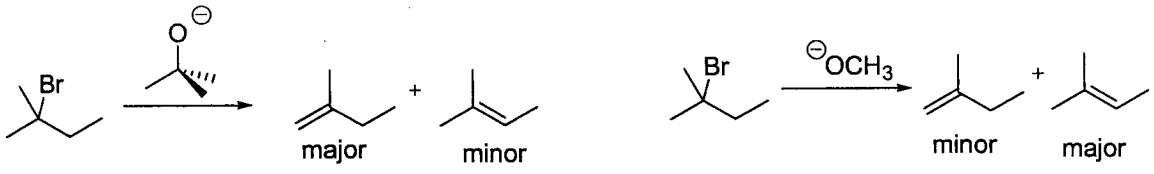
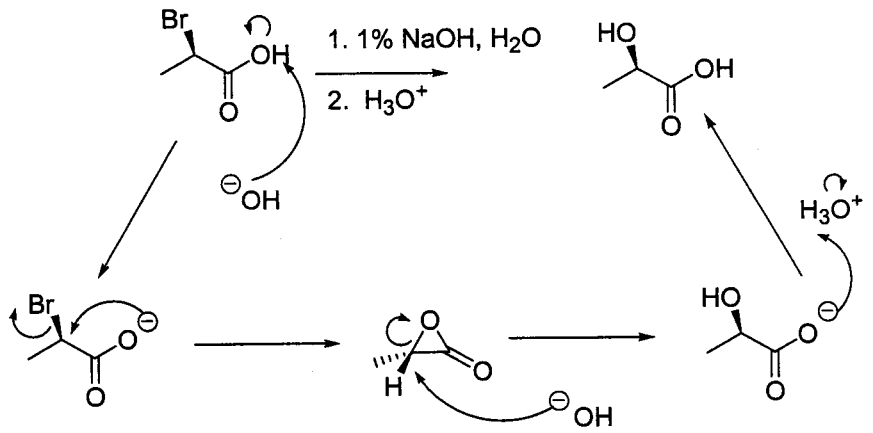


6. Propose a mechanism:



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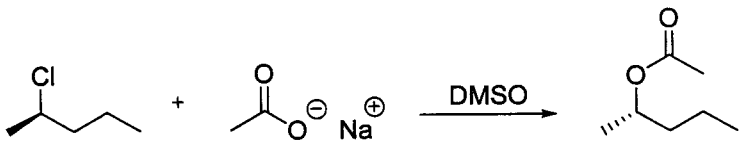

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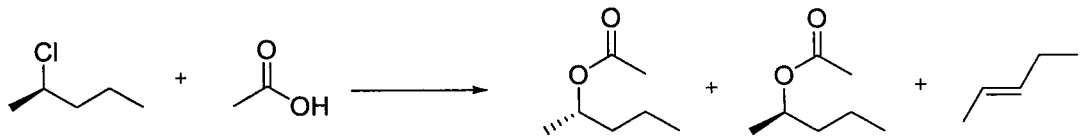
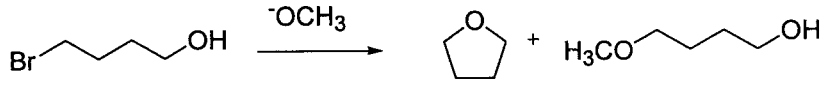
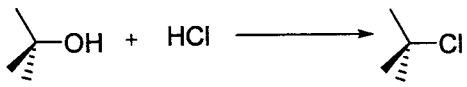


9.



10. Explain why t-butanol will not react with potassium chloride, but will react with concentrated HCl to form 2-chloro-2-methylpropane.

But



OH is not a good leaving group, but HCl can protonate to make  which is. Now a S_N1 reaction will proceed.