

March 1, 2017: Nucleophilic substitutions S_N1 and S_N2

Homework: Solve problems 6.3, 6.4, 6.7, 6.11, 6-12, 6.14-6.15

1. S_N2 reaction. Orbitals involved in formation and breaking of bonds (Ch 6.6)

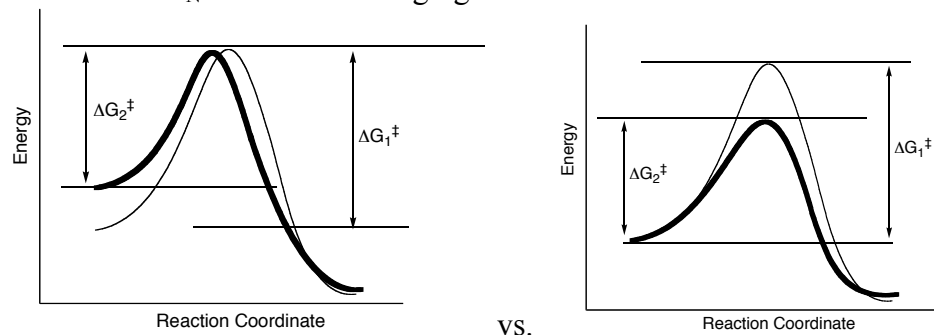
2. The mechanism of the S_N2 reaction (Ch 6.8 and box, page 253) and S_N1 reaction (Ch. 6.9)

3. Transition state theory (Ch. 6.7). Hammond Postulate (Ch. 6.13A). Two step mechanism with intermediate. Difference between **intermediate** and **transition state**.

https://en.wikipedia.org/wiki/Transition_state_theory

4. Structure activity relationships (S.A.R.) in S_N2 reaction: Changing the nucleophile Nu: (Ch. 6.13B).
Better Nu: is less stable Nu: For same Nu-atom, better Nu: has higher pK_A of its conjugate acid NuH

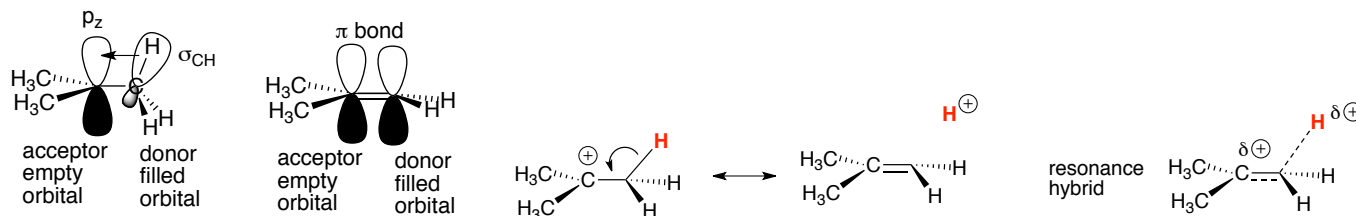
5. S.A.R. in S_N2 reaction: Changing the solvent



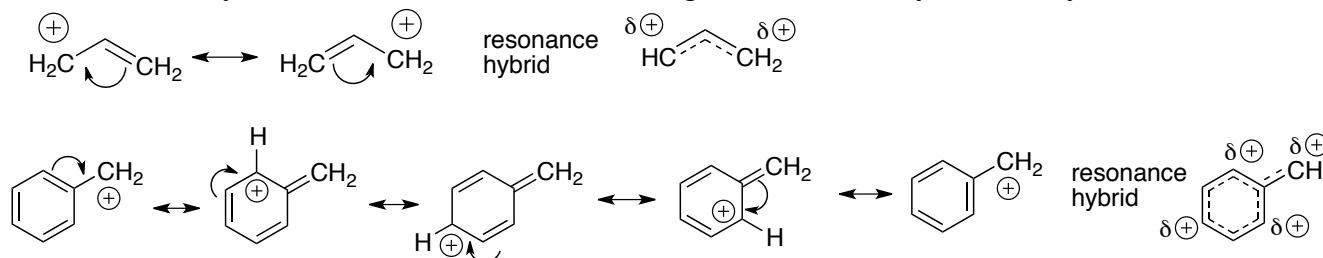
6. S.A.R. in S_N1 / S_N2 reaction: Changing the electrophile from primary, to secondary to tertiary.

7. Mechanistic origin of S.A.R. in S_N1 : Carbocation. Structure. Stability (Ch. 6.11)

3.1. 3° Carbocation is stable due to Hyperconjugation a.k.a. “no bond resonance”



8. Stabilization by resonance—via double bond acting as donor—in **allyl** and **benzyl** carbocations



9. Side-by-side comparison of S.A.R of S_N1 and S_N2 reactions (Ch. 6.13 and page 271)

4.1 Polar protic solvent stabilizes carbocation. Hammond postulate predicts that stabilization of carbocation also stabilizes TS (“product-like TS”). Lowering of TS accelerates S_N1 reaction

Note: S_N2 is the opposite: polar protic solvents slow down S_N2 by stabilizing the Nu:

4.2. Better leaving group makes S_N1 faster (just like S_N2)

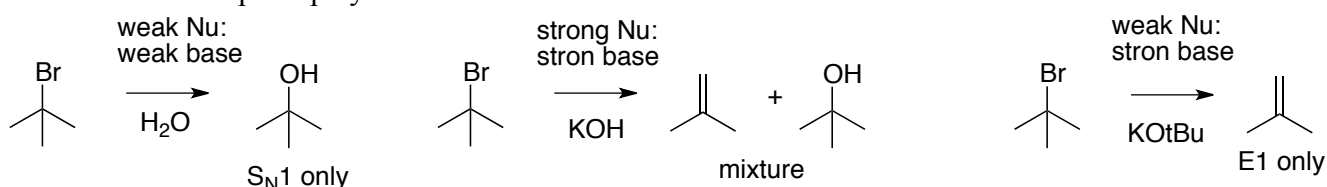
4.2 Nucleophile plays no role in S_N1 , but *better nucleophile (less stable Nu:) is better for S_N2*

March 3, 2017: Nucleophilic substitutions S_N1 and S_N2 . Eliminations E1 and E2

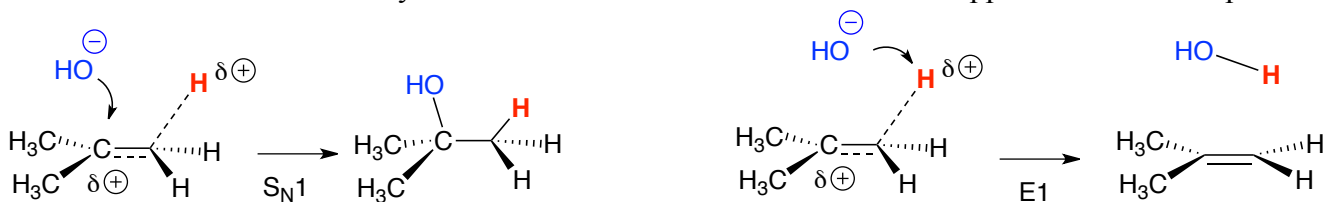
Homework: Solve problems 6.20, 6.22, 6.25, 6.26, 6.29, 7.4, 7.6, 7.7

1. Structure-reactivity relationships of S_N1 reaction (Ch. 6.13 and page 271)

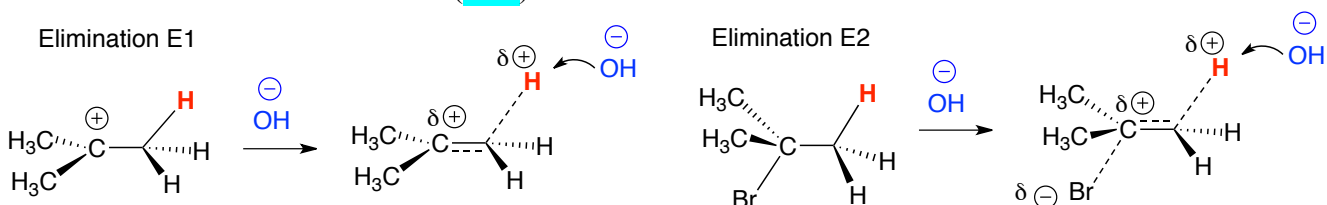
4.2 Nucleophile plays no role? *Or does it...*



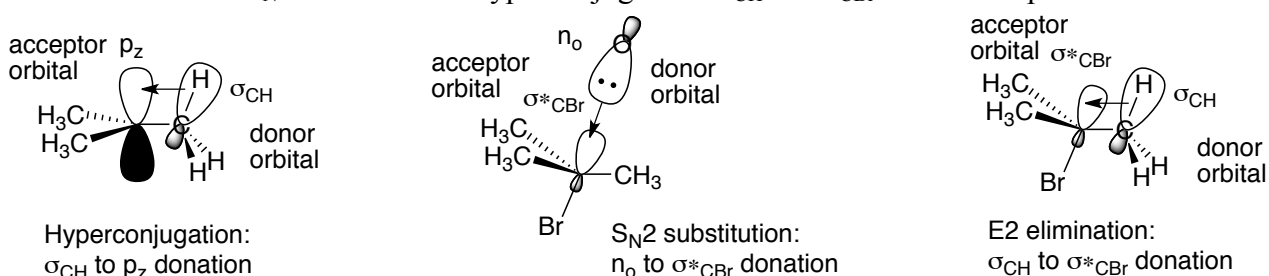
2. E1 reaction mechanism. Very similar to S_N1 but attack on carbocation happens in a different place



3. Another kind of elimination: E2 (6.16)

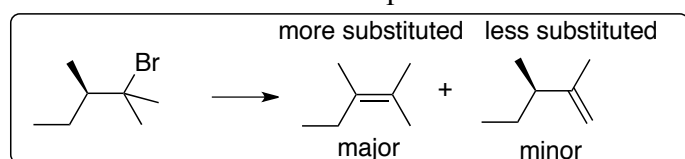


4. Mandatory anti-periplanar arrangement of Br and H for E2 elimination (Ch. 7.6D). E2 elimination has elements from S_N2 reaction and Hyperconjugation. σ_{CH} to σ^*_{CBr} interaction pre-forms the π -bond



5. Mechanistic significance: strong nucleophile favours substitutions, strong base favours elimination.

6. E1 and E2 reactions in complex substrates. Zaitsev Rule: Form more substituted alkene (Ch. 7.6)



E2 elimination obeys Zaitsev rule and it forms only products that obey anti-periplanar transition state

