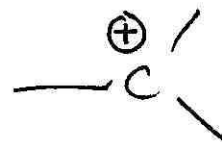


S45. Carbanions & Carbocation

S45.0



Summary

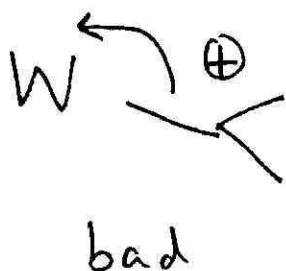
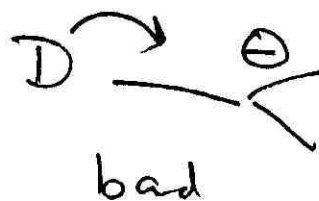
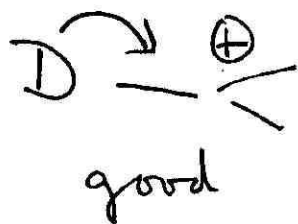
Electron donors stabilize carbocations.

Electron donors destabilize carbanions.

Electron withdrawing groups stabilize carbanions.

Electron withdrawing groups destabilize carbocations.

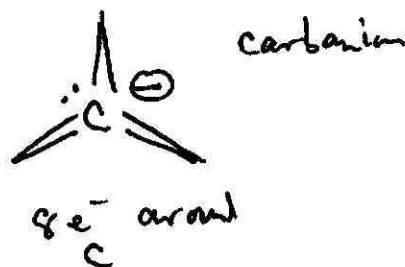
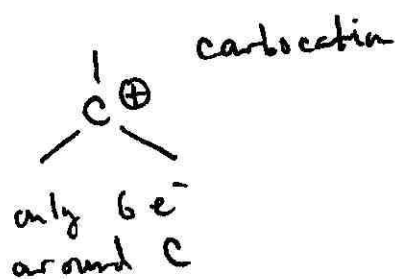
or



Carbocations, carbanions, electron donating and electron withdrawing groups 545.1

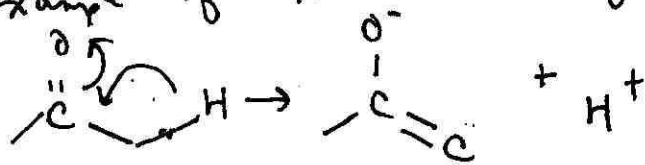
① This is an extra lecture. I am writing this lecture down, not because you'll have time to learn this material in this class, but because, I think just a little more background will help the interested student appreciate how the organic chemistry you will study next year is properly embedded in MO theory, that is the quantum theory of the electron.

② One of the key ideas you will learn next year are that "reactive intermediates" are essential in understanding the course of organic reactions. Two such intermediates are carbocations and carbanions



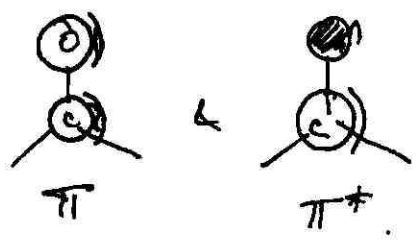
Both carbocations & carbanions are reactive (i.e., unstable). Lots of organic reactions take place with these as intermediates.

③ The key to a lot of organic chemistry reactions is the positioning of neighboring groups which help stabilize the carbocation and carbanion state. These groups are generally either electron donating or electron withdrawing (see lecture 26). A good example of the e⁻ withdrawing group was the carbonyl.



④ Taken from an MO viewpoint we reduce the effect of the $\overset{\text{O}}{\parallel}{\text{C}}$ to a single orbital. We then see if this orbital is occupied or empty. If it is occupied \Rightarrow the unit behaves as an e^- acceptor or σ withdrawer. If this single MO is filled the unit behaves as an e^- donor.

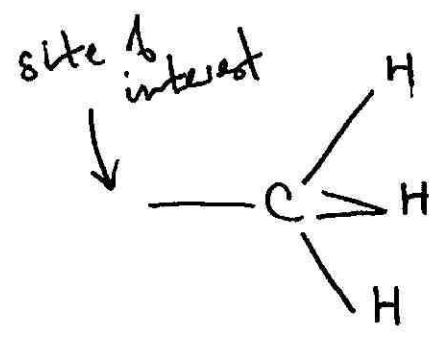
In the case of $\overset{\text{O}}{\parallel}{\text{C}}$ we have



As the π^* is located on the C, at the connected end of this moiety, $\overset{\text{O}}{\parallel}{\text{C}}$ behaves as an e^- acceptor:

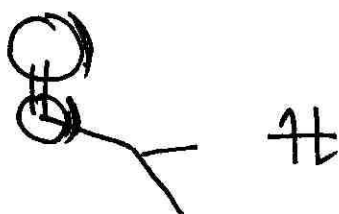
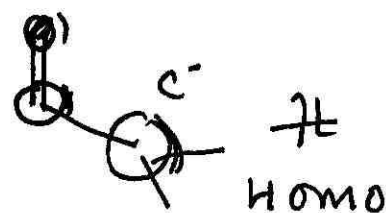
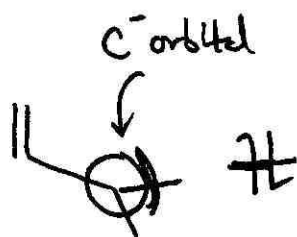
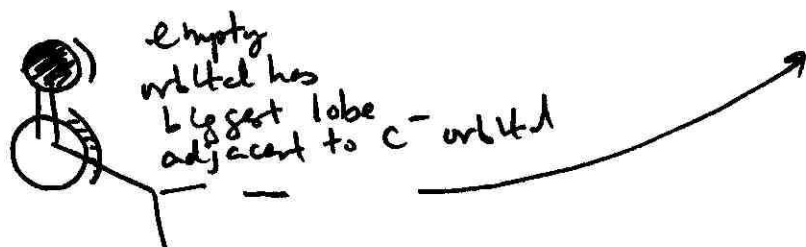
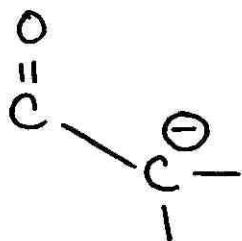
is the key orbital in $\overset{\text{O}}{\parallel}{\text{C}}$'s chemistry (at least as a σ bonded ligand).

⑤ With the same logic we can consider the CH_3 and CF_3 group. For simplicity let's see the effect of these groups on a " π " A.O. of C, using only a σ bonding picture to either H or F.



The orbitals of interest are:

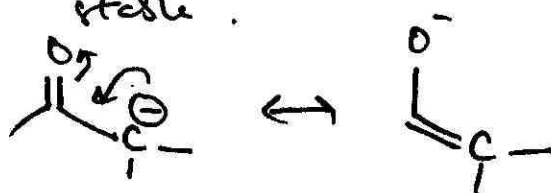
Electron withdrawing group.



As empty orbital is closest (spatially) to C⁻ orbital its interaction is most important.

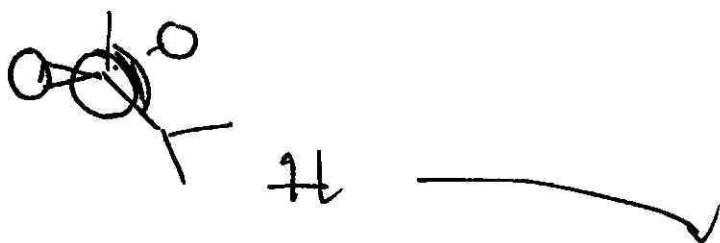
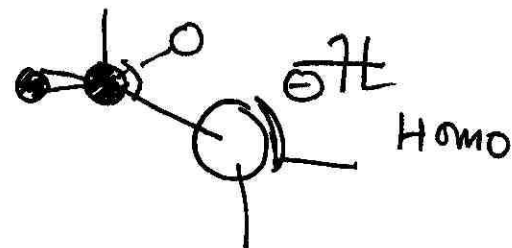
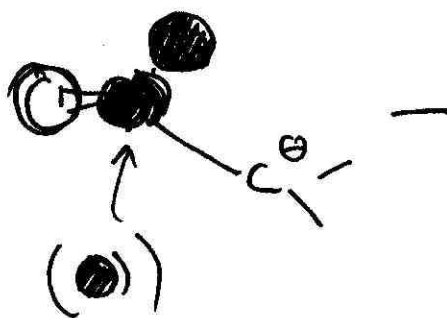
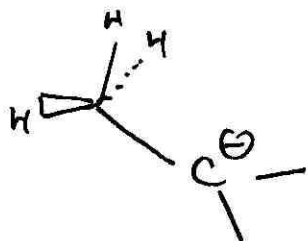
∴ HOMO is stabilized & the molecule is less reactive i.e., more stable.

By arrows



Electron donating group

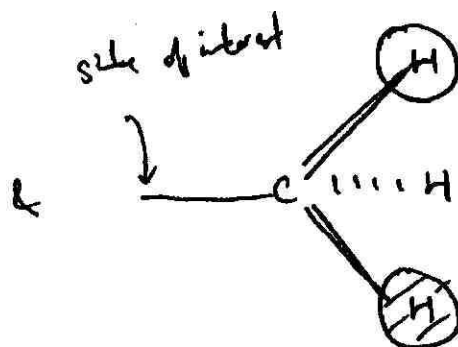
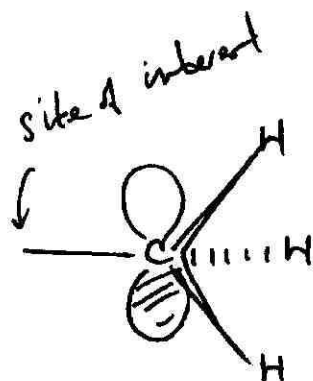
S 45.2c



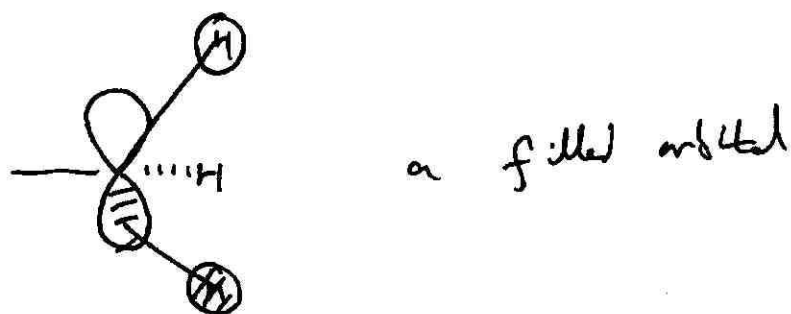
H is more electropositive than C. \therefore filled orbital is mainly on C of CH_3 -unit.

\therefore HOMO is destabilized; molecule is more reactive; molecule is less stable.

Electron donating groups destabilize carbanions

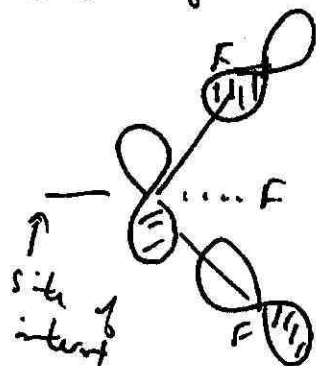


As H is more electropositive than C $-CH_3$'s orbital which is C-based is



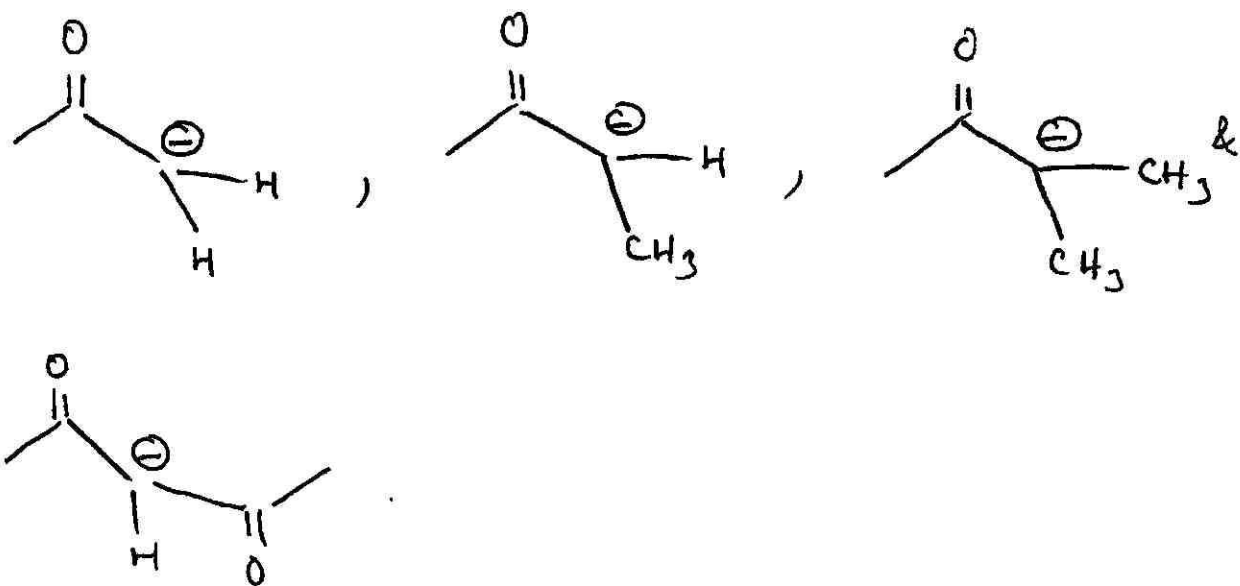
& hence $-CH_3$ is an electron donor.

⑥ By the same logic for $-CF_3$ the orbital of interest is



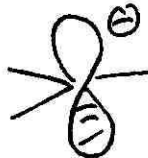
& $-CF_3$ is an e^- withdrawer.

⑦ Let's use this logic to consider the stability of the following carbanions:




⑧ In each of these reactive intermediates we are dealing with an anion orbital which looks like



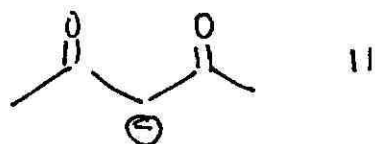
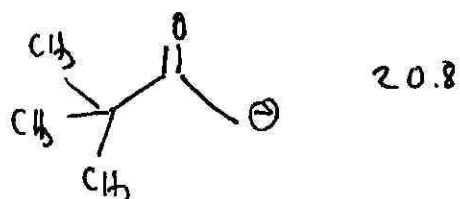
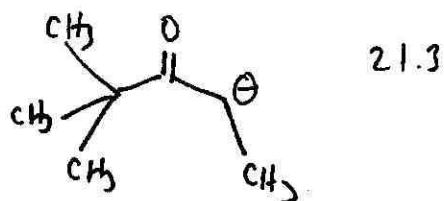
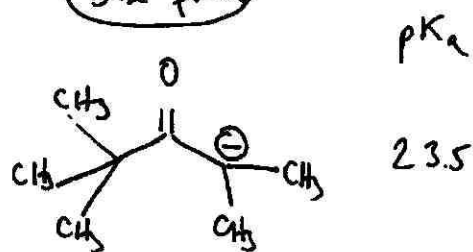
⑨ For simplicity we'll consider the  picture. This is a filled non-bonding orbital. Lowering the energy of this orbital will stabilize the system (a lot). Raising the energy of this orbital will destabilize the system a bit.

(10) Conclusion:  stabilizes anion CH_3COO^-

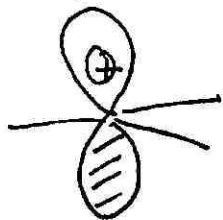
 destabilizes anion.

(base form)

(11) Data:

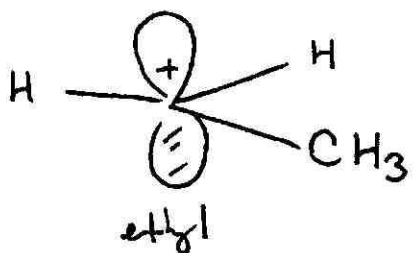


(12) In exactly the same way we can consider carbocation.

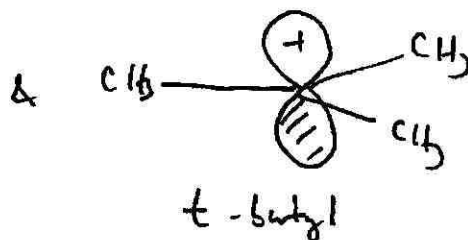
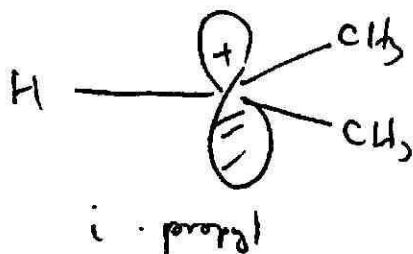


note here the orbital is empty.

If this orbital has a nearby ^{occupied} orbital which is high in energy then the carbocation is stabilized.

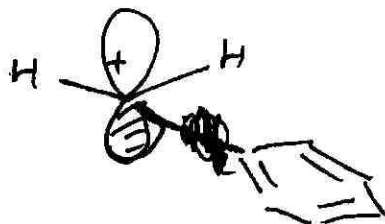


vs.



(13) In t-butyl group there are more nearby occupied orbitals (recall -CH₃ is an e⁻ donor) & hence t-butyl is the most stabilized.

(14) But better yet will be

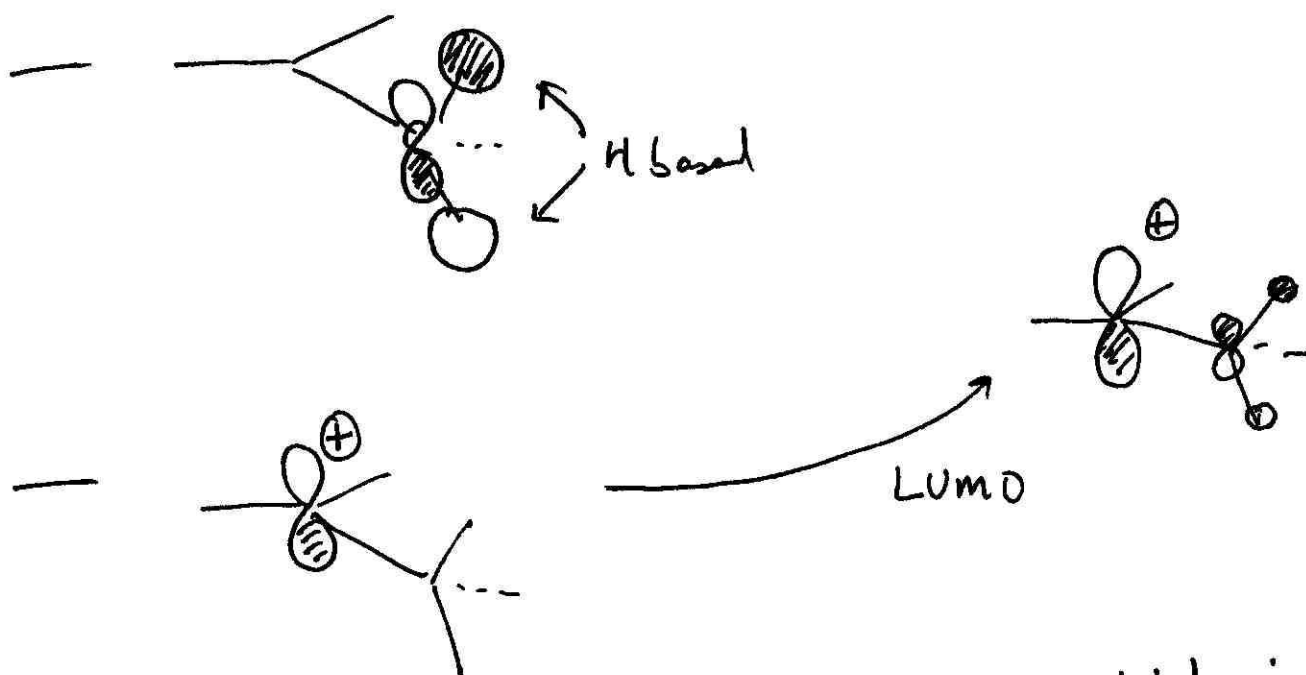
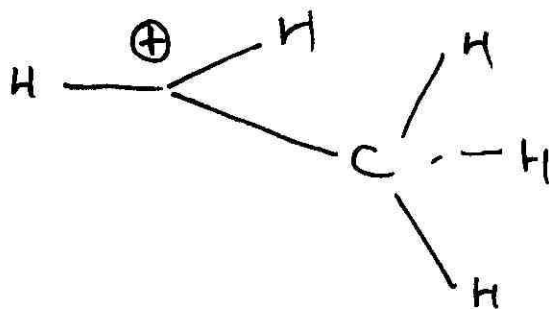


Here we have the very high energy benzene HOMO.

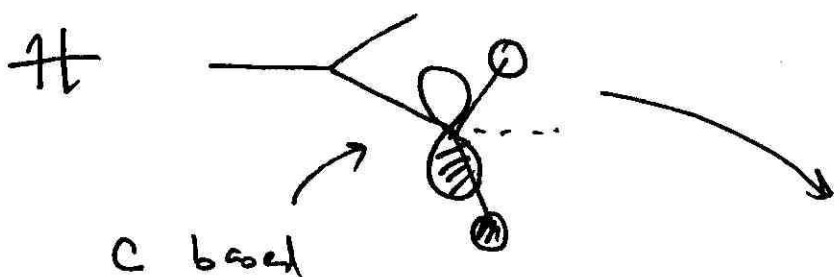
Carbocation.

S45.6b

Key orbital in reaction is the LUMO
(carbocations are Lewis acid)

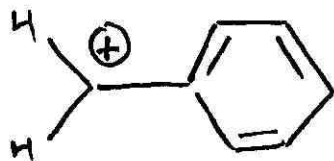


LUMO is higher in energy. \therefore Less reactive
 \therefore molecule is more stable.

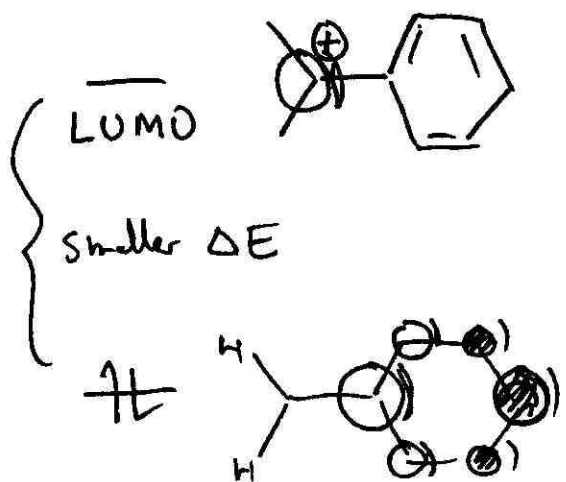
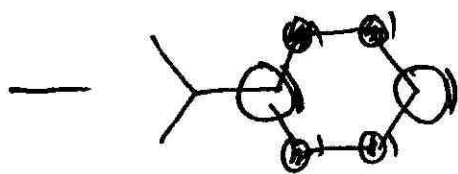


Carbocation w/ aromatic ring

S45.6c



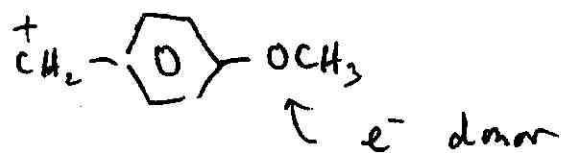
C^{\oplus} is more electronegative
(a lot more electronegative) than
C neutral



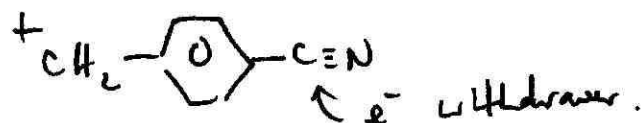
LUMO is
stabilized &
molecule is more
stable

⑮

Now we can place e^- density groups or e^- withdrawing groups into the benzene ring.



or



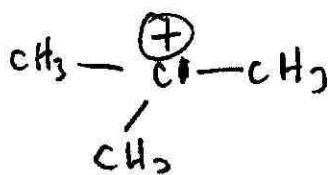
Data

(no numbers)

I. P.



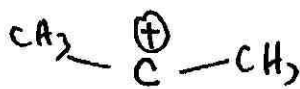
660 kcal/d



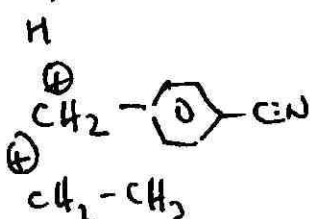
715 kcal/d



748 kcal/d



760 kcal/d

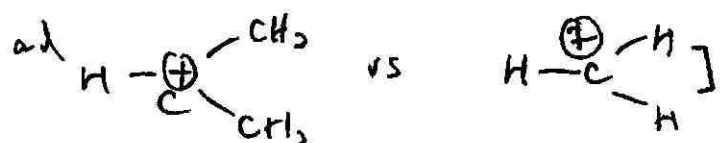
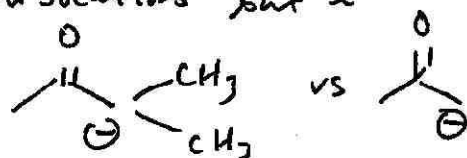


806 kcal/d

835 kcal/d

$$^{\oplus}CH_3 \quad 950 \text{ kcal/d.}$$

(16) Note there is an easy mnemonic for this material. e^- donors stabilize carbocations but e^- donors destabilize carbanions. [Recall



& e^- withdrawers stabilize carbanions but destabilize carbocations. & that's the way it will be taught next year.