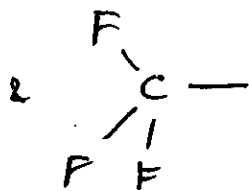
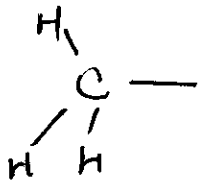


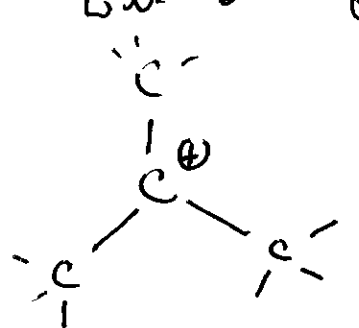
Addition to 45

Lecture 45 is on the effect of groups such as  $\text{H}$  and  $\text{F}$  on carbocations & carbanions.



The treatment of the orbitals in this lecture were based on MOs without much use of localized orbitals. But given the material we have just covered a localized treatment leading to the MO interaction will be quite useful.

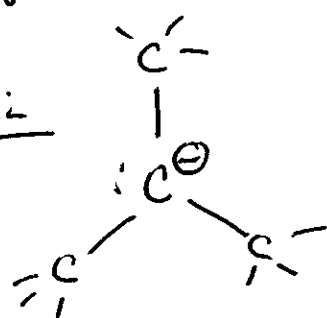
② Carbocation



$sp^2$   
trigonal planar

$6e^-$   
around central  
C

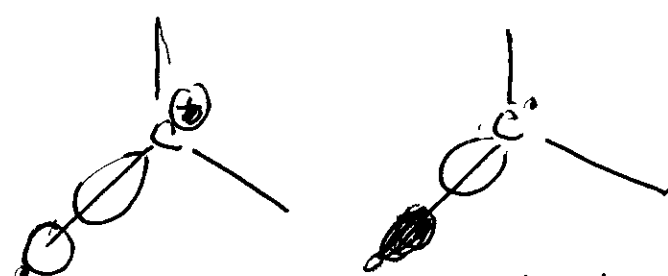
carbanion



$sp^3$   
trigonal pyramidal

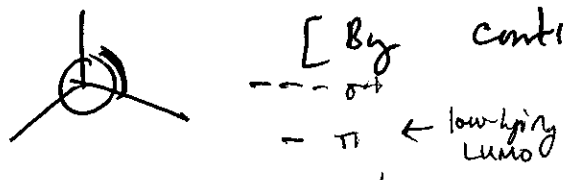
$8e^-$   
around central  
C

③ Carbanion Carbocation

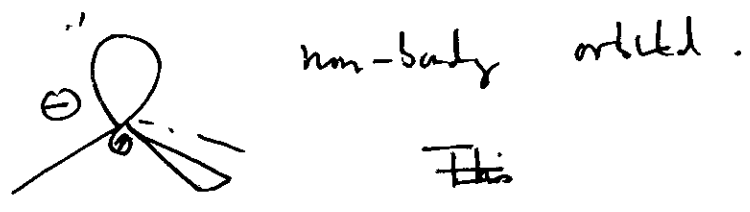


$\sigma$  localized bonding orbitals along their  $\sigma$  bonds  
 " " antibonding orbitals " " " "

④ The key orbital here is the LUMO : a non-bonding p orbital  
 [By contrast HOMO is a bonding  $\sigma$  orbital]

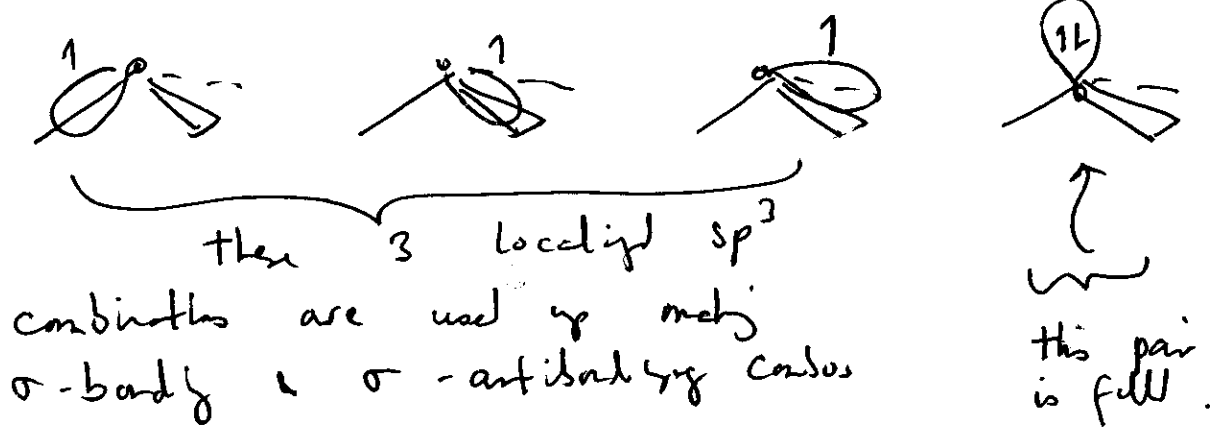


⑤ For carbanions, the central carbon is  $sp^3$ . There are bonding localized orbitals along the  $\sigma$ -bonds, antibonding localized orbitals along the  $\sigma$  bonds & the key orbital is the non-bonding  $sp^3$  orbital.

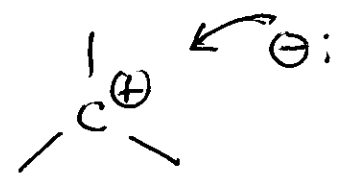


$C^-$  has 5 valence electrons

Note  
 ---  
 # n.b.  
 # # #



⑥ Therefore carbocations are electrophiles



& carbanions are nucleophiles

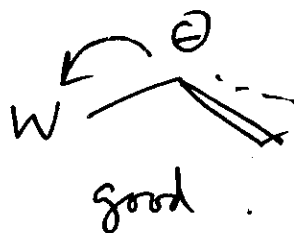
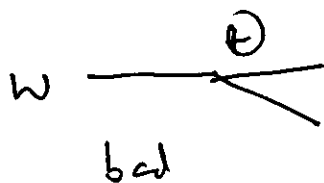
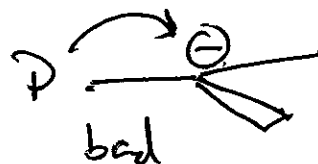
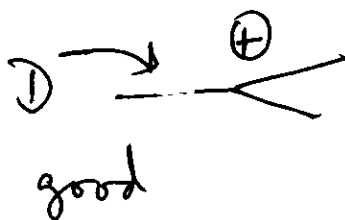


⑦ Electron donors stabilize carbocations

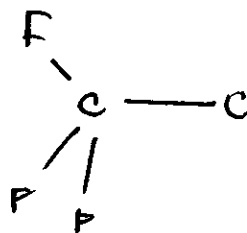
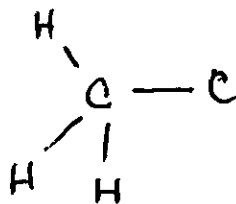
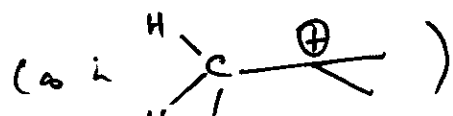
Electron withdrawers " carbanions

Electron donors destabilize carbocations

" withdrawers " carbanions

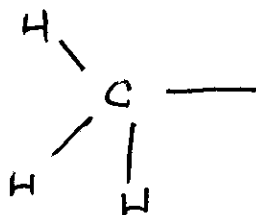


⑧ Now let's consider

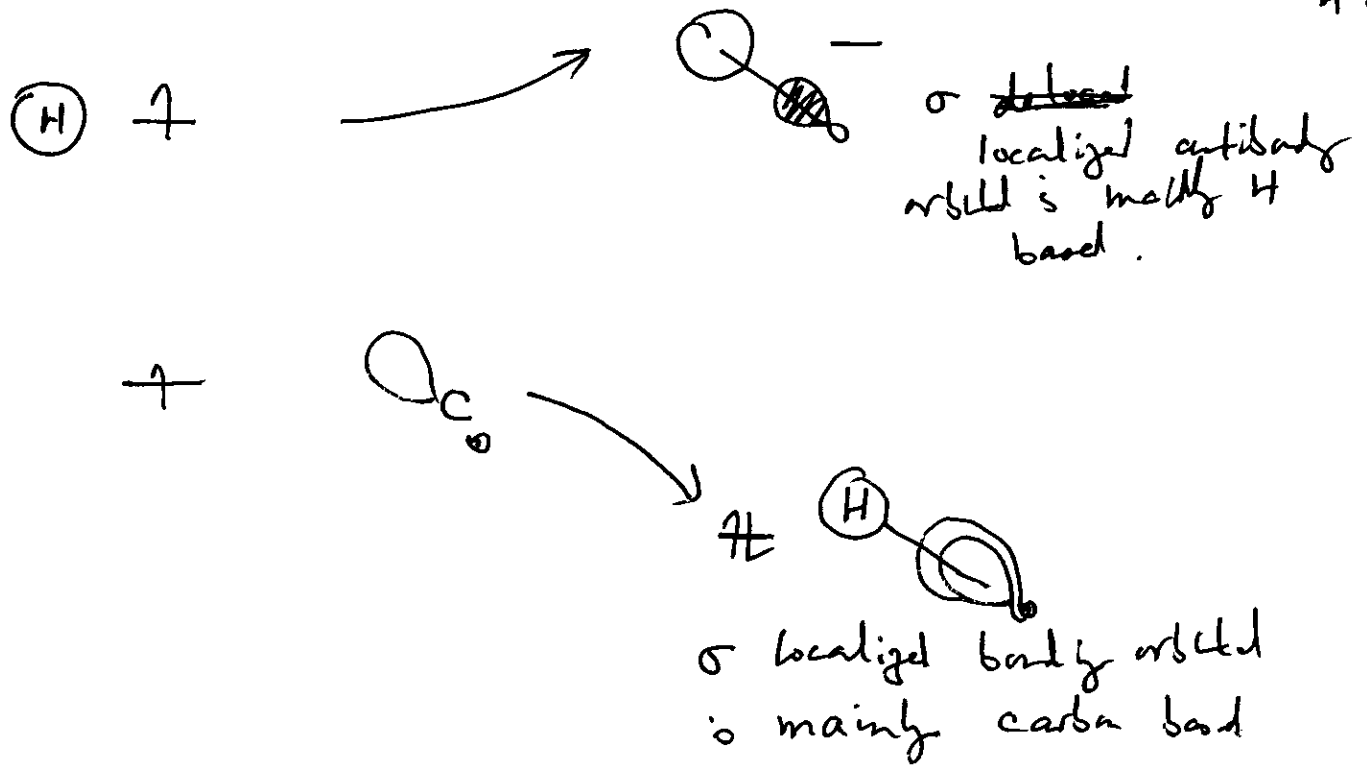


These carbons are both  $sp^3$ . There are  $\approx$  4  $\sigma$  bonds to the central C. There are  $\therefore$  4  $\sigma$  bonding localized orbitals & 4  $\sigma$  antibonding localized orbitals.

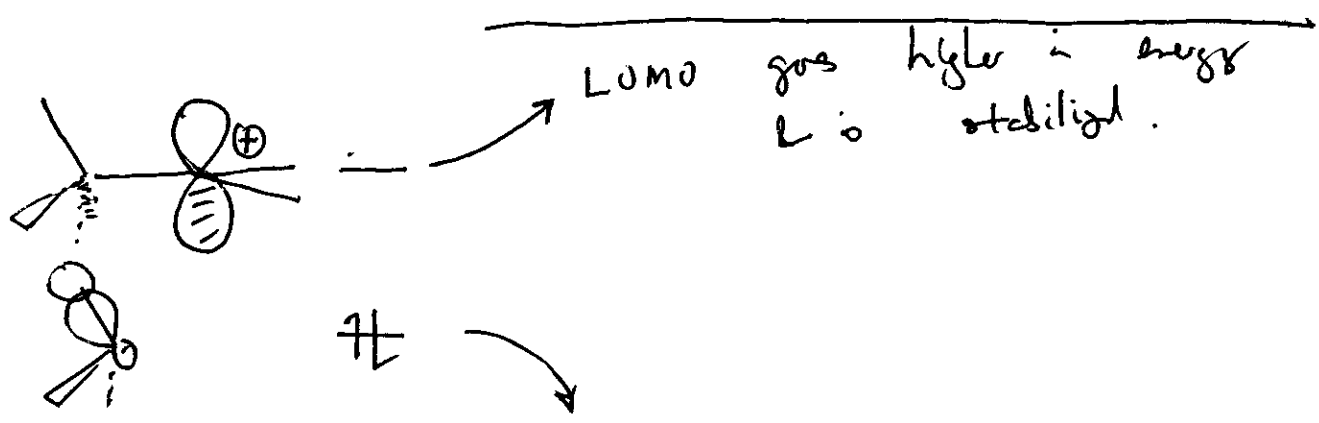
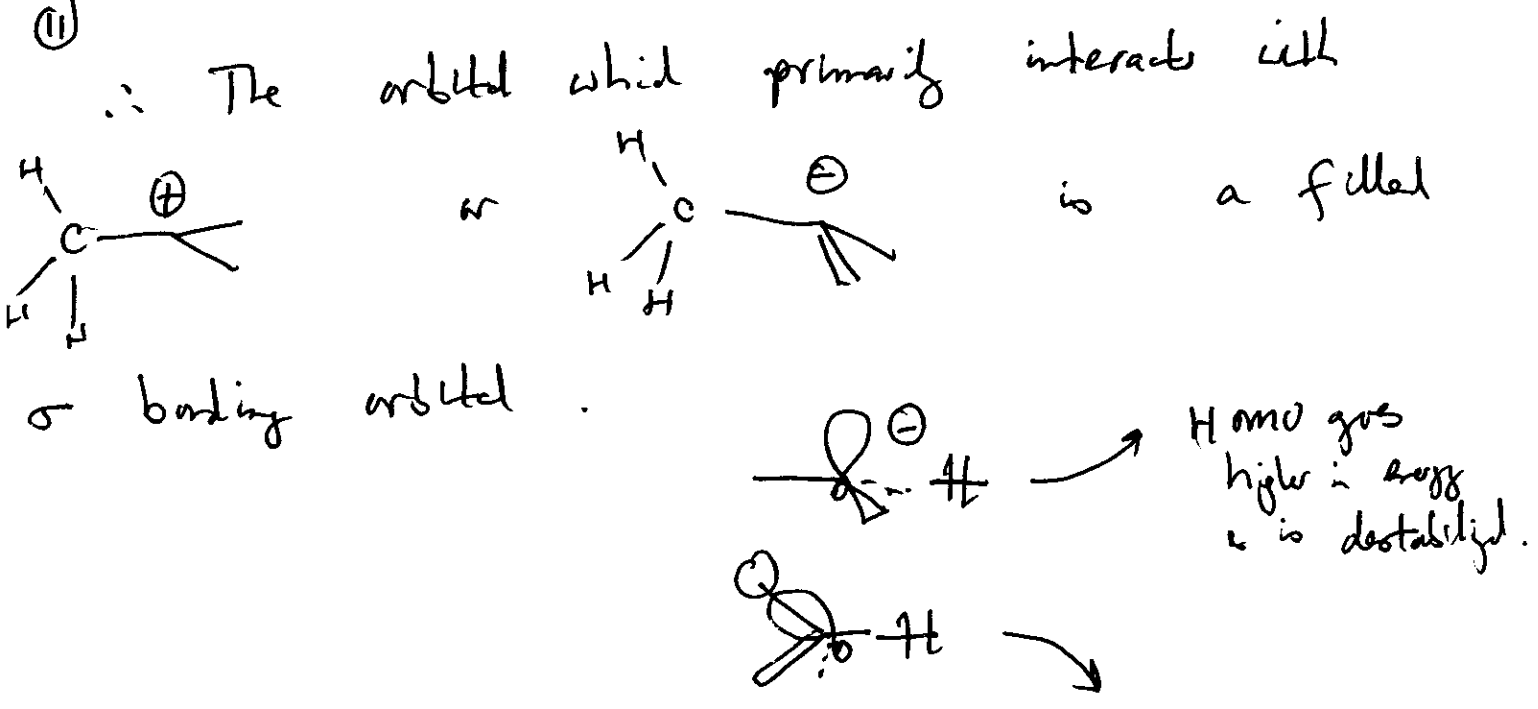
⑨ Let's first consider



(10)

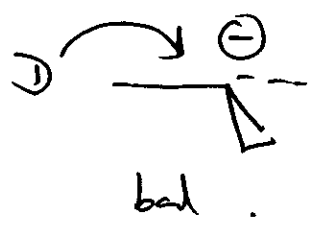
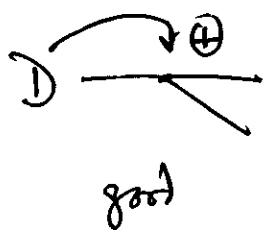


(11)

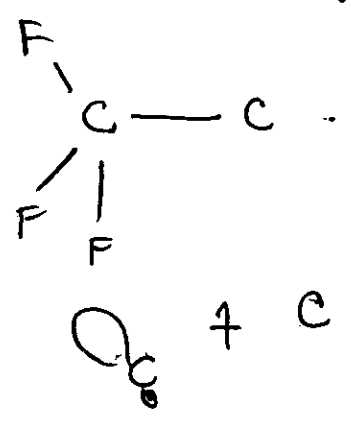


CH<sub>3</sub> group stabilizes carbanion

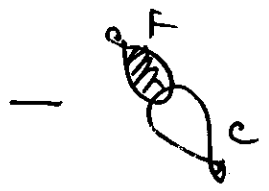
carlocation is a destabilizing group



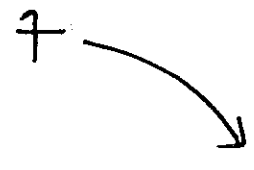
In exactly the same way we can treat



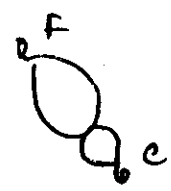
Here



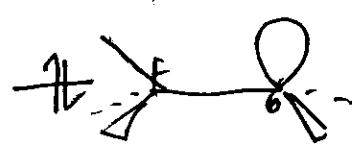
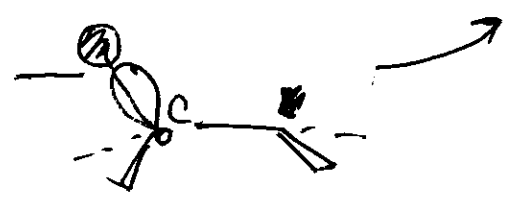
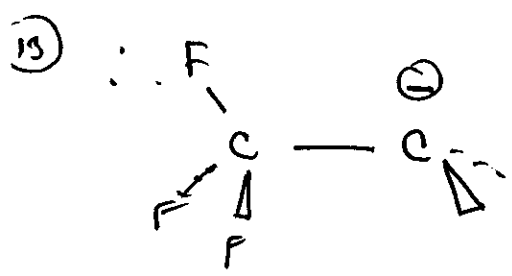
LUMO is carbon bad



H

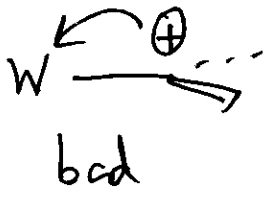
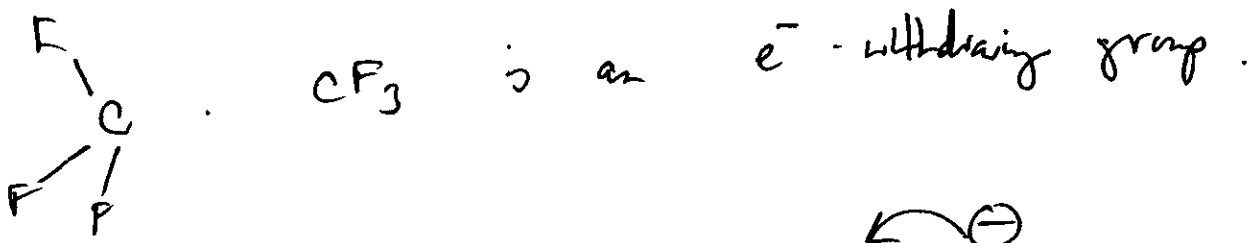


F-bond

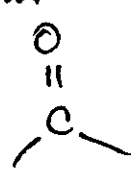



HOMO is stabilizing

(14) &  LUMO is destabilized by

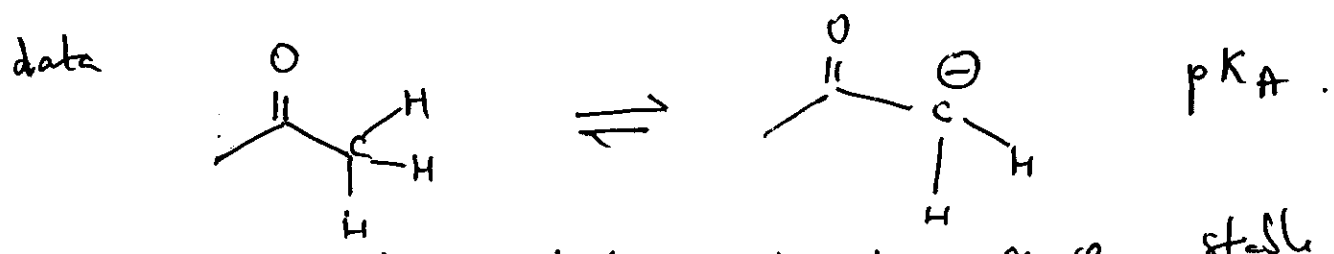


(15) ~~Data  $pK_A$  of the following acid base reactions~~

We can add  $CH_3$  (D) &  $CF_3$  (W) to our previous knowledge of  $e^-$  withdrawing groups  
 (W as key orbital was  $\pi^*$  ) &  
 electron density group

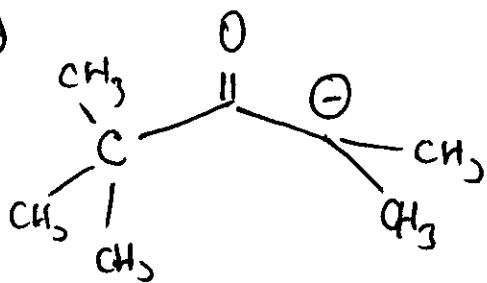
$CH_3O^-$  (D as key orbital is O lone pair which is filled).

(16) Let's use this data to rationalize the following

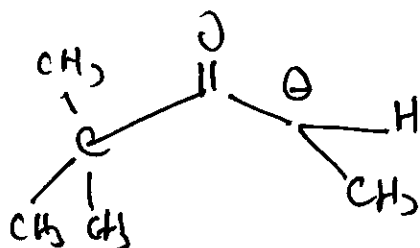


When  $pK_A$  is low ~~is~~ anion is more stable  
 " " " high " " less stable.

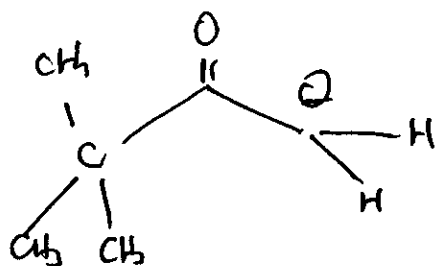
(17)

pK<sub>a</sub>

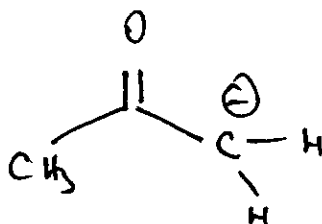
23.5



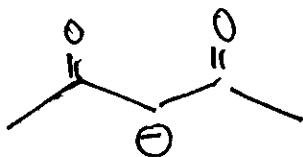
21.3



20.8



20



11

$\text{O}=\text{C}$  is W &  $\text{CH}_3$  is D.

