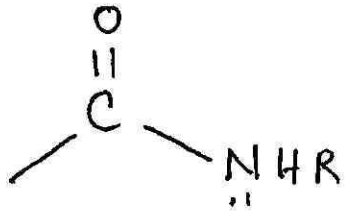
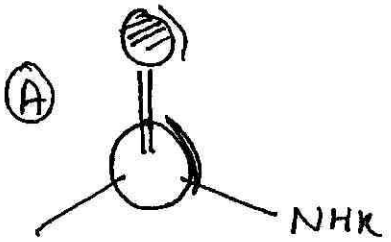
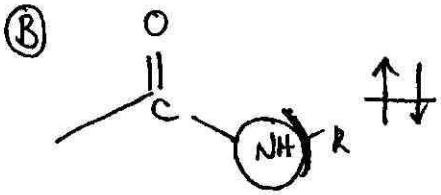
Lecture 26 — Electron donating groups and electron withdrawing groups

① Let's consider  , an electrophile



LUMO (before including N) —



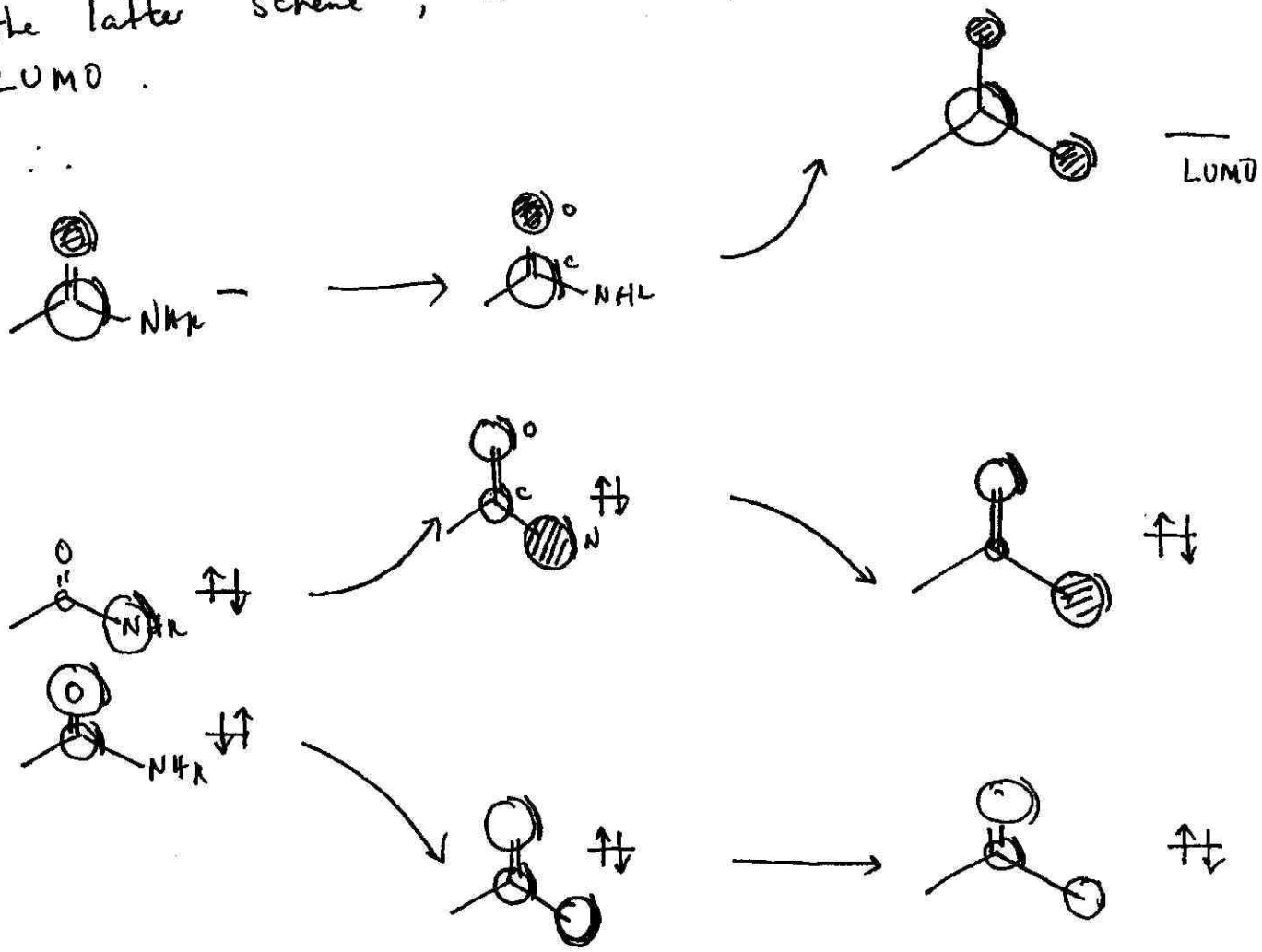
② Because an amide is an electrophile, we are interested in its LUMO. We will find an approximate LUMO by pair-wise mixing.

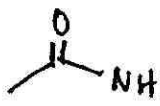
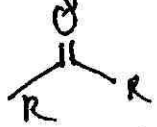
Should we first interact (B) with (C), then the new (B) with (A) or should we interact (A) with (B), then the new (B) with (C)?

③ Answer:

As we are interested in describing the LUMO as well as possible, the former scheme is better. In the latter scheme, the 2nd step does not even affect LUMO.

∴



The LUMO of  is higher in energy than  ∴ amide is a <u>worse</u> electrophile than ketone.

④ Putting this result together with alkene result:

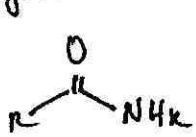
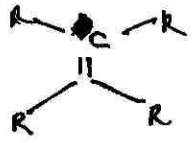
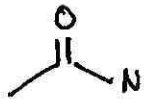
Best electrophile  >  > 

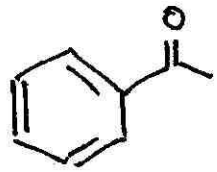
TABLE 19.3 The ease of reduction of various functional groups with $LiAlH_4$ in ether[489]

However, $LiAlH_4$ is a very powerful reagent, and much less chemoselectivity is possible here than with most of the other metal hydrides

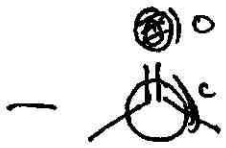
Reaction	Substrate	Product	
6-25	RCHO	RCH_2OH	Easiest
6-25	RCOR	RCHOHR	
9-45	RCOCl	RCH_2OH	
9-42	Lactone	Diol	
0-80		RCH_2CHOHR	
9-42	RCOOR′	$RCH_2OH + R'OH$	
9-38	RCOOH	RCH_2OH	
9-38	$RCOO^-$	RCH_2OH	
9-39	$RCONR'_2$	$RCH_2NR'_2$	
6-27	RC≡N	RCH_2NH_2	
9-47	RNO_2	RNH_2	
9-67	$ArNO_2$	ArN=NAr	Most difficult
5-9	RCH=CHR		Inert

⑤ When we worked out the properties of the amide,  we considered the filled π-orbital of the N atom. Since we considered the effect of a filled orbital (with a pair of electrons) this is called an electron donating group. $-\ddot{N}HR$ is electron donating. So is $-\ddot{O}R$ or $-\ddot{O}H$.

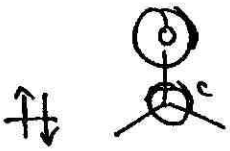
⑥ If we were to look at the effect of a carbonyl ()



then we would have to consider the effect of two orbitals



note the unfilled orbital is principally on C



note the filled orbital is principally on O.

As it is the carbon atom which is bonded to  it is the unfilled orbital which affects the  ring the most.

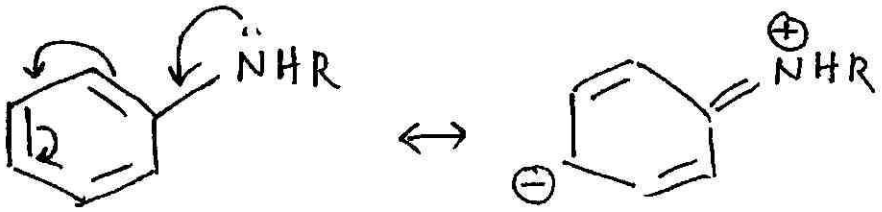
As it is an unfilled orbital we call it the opposite of an electron donating group, we call it an electron withdrawing group.

⑦ Summary

electron donating

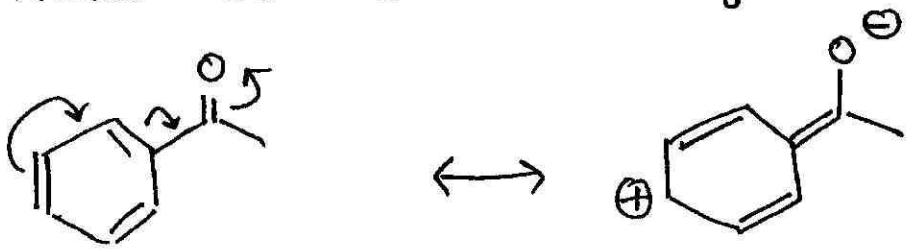
electron withdrawing.

⑧ Remember organic chemists want to turn the orbitals into arrows. So an organic chemist thinks about electron donating and electron withdrawing in the following way:

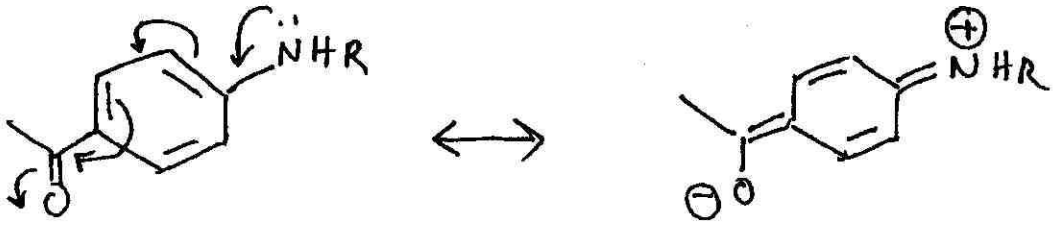


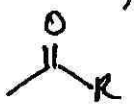
NHR is electron donating

⑨ While electron withdrawing is seen as :



⑩ Putting these two ideas together



⑪ From the MO perspective, we think of the effect the LUMO of  and the HOMO of –NHR have on the full molecule's MO.