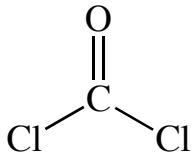
Exercise 107 - Reactivity

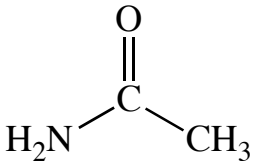
Question

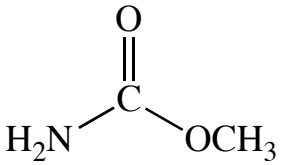
Consider the follwing functional groups and rank them in order of decreasing reactivity. Explain your reasoning.

i)

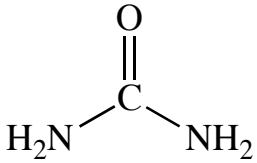


Phosgene





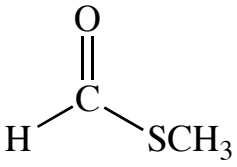
A carbamate.

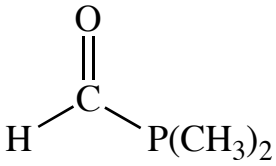


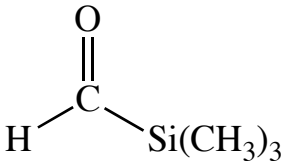
Urea

In our discussion of the reactivity of CADs, it came down to the degree to which the functional group is stabilized by resonance delocalization of the lone pair on the heteroatom. The less electronegative the atom the better the amount of delocalization. In this series, three of the functional groups have TWO substituents that can delocalize electrons into the CO bond. If one such atom stabilizes the CO then two should be better. Chlorine, however, is not at all effective at stabilizaing CO and two such atoms is no better making phosgene the most reactive. Followed by the amide, the carbamate and the urea.

ii)

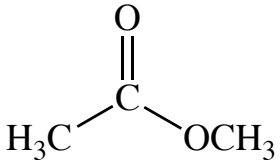


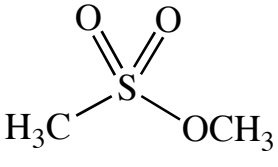


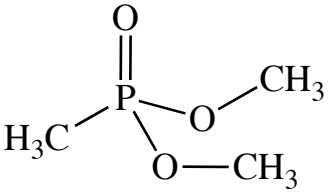


This is a bit of a stretch, to be honest. Based on the reasoning we used in class one might predict that the acyl silane would be most reactive since it cannot be stabilized by resonance (there is no lone pair on Si). Of the remaining two, P is less electronegative than S so by analogy with ester and amide, should be less reactive. Having said that, acyl phosphines and silanes are not very common so I have no real sense of how reactive they actually are.

iii)

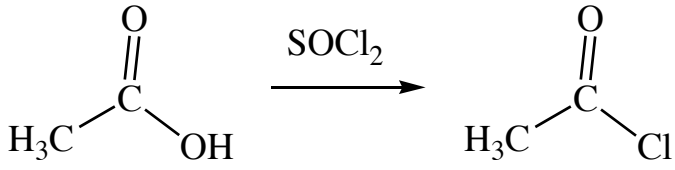




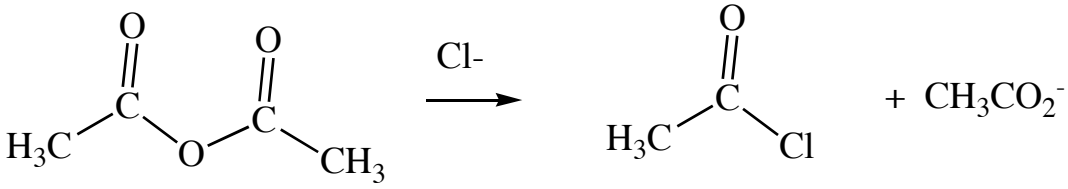


Again, if we consider the resonance arguement, the sulfonate ester would be most reactive because the lone pair on OCH3 is spread over two S=O bonds. The phosphonate would be least reactive because it has two lone pairs that can be delocalized into the P=O bond.

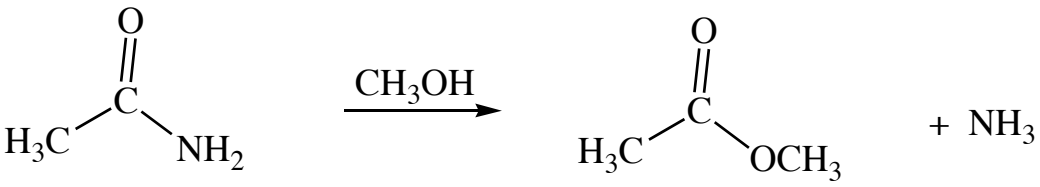
Question
Some the following reactions won't work. Which ones and why?



OK.



This reaction fails because the acid chloride is more reactive than the anhydride. The reverse reaction is favoured here.



The ester is more reactive than the amide so once again the reverse reaction is favoured.